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THE CHEMICAL HETERODYNAMICITY OF NASCENT HYDROGEN. II.

A. K. Dmitriev

In my first report [1], I set forth the following conclusions: a) the chemical activity of nascent hydrogen varies widely, depending upon the nature of the metal at whose surface the hydrogen is evolved when the metal is dissolved in acid; and b) there is a periodicity in the change of hydrogen's chemical activity.

Although these conclusions were based upon experimental findings, these findings were not very diversified, as the substances subjected to hydrogen reduction were confined to sulfur and its compounds. Further research, therefore, required the extension of this group of substances to compounds of different composition and structure.

Increasing the number and diversity of substances suitable for this objective entailed considerable difficulty, inasmuch as their selection involved various restrictions: nonvolatility, not decomposing at 100°, feasibility of a quantitative control of the reduction process, feasibility of reduction with hydrogen but not with metals, which involved the necessity of choosing compounds with covalent bonds, and so forth. That is why it proved advisable to confine our choice to organic compounds possessing a bright color, the following being selected from the long list of such compounds: methyl red, methylene blue, pyronine, and indigo carmine.

The principal advantage of colored substances is that many of them are decolorized when reduced, thus serving as their own indicators of the end of reduction; this is extremely convenient, since the change of color during reduction is easily followed, eliminating the tedious determination of the reduction products.

Our choice of the four specified colored substances was dictated by considerations of diversity of composition and structure and by the differences in their chromophore groups.

Another objective of the present research has been a study of metallic alloys; this is of practical and theoretical interest, as may be seen from what follows.

EXPERIMENTAL

The series of reduction tests was run as follows: a standard volume of a solution of an organic compound, of given concentration, was poured into a beaker, a certain volume of 1:1 hydrochloric acid was added, and the solution was heated to a gentle boil on an electric hot plate, after which the metal was added in powder form to the solution gradually, in small portions, until the colored solution was decolorized as the result of reduction by hydrogen. Then the residual unused metal was weighed, the difference between this weight and that of the original sample giving the quantity of metal required for the reduction of the organic compound by nascent hydrogen.

Our research has established that these tests were fully reproducible and that very different amounts of different metals were required to decolorize a given volume of solution of the colored substance, thus confirming our basic conclusions regarding the far-reaching chemical heterodynamicity of nascent hydrogen.

TABLE 1

Reduced substance	Mg	Zn	Al	Mn	Cd	Fe	Co	Ni
Methyl red	6	11	90	54	360	250	410	875
Methylene blue	3.5	13	138	100	190	225	300	465
Pyronine	2.5	10	58	50	–	60	230	300
Indigo carmine	2.5	10	70	45	–	50	150	300
KCNS	2	30	50	54	80	125	400	750

In Table 1 we give the results of four series of tests, expressed not in weights of the various metals, but recalculated and expressed in milliliters of the volume of colored solutions that can be decolorized by the dissolution of 1/24th gram-equivalent of

each metal. It is obvious that the greater the volume of solution decolorized, the more active the hydrogen.

The last line gives, by way of comparison, the indexes of hydrogen activity secured in a reaction with KCNS, as stated in our first report.

Methyl red is only very slightly soluble, so that we used a saturated solution in the tests. The concentration was higher for the other dyes: 1.8 g liter for methylene blue, 1.5 g for pyronine, and 1 g for indigo carmine.

Reduction was very smooth, the color of the solution gradually growing paler until it vanished completely, except in the case of indigo carmine, the solution of which changed from dark blue to slightly greenish, which corresponds to a leuco compound, according to the literature, though other shades were sometimes visible.

In regarding the figures listed in Table 1 as a singly-valued index of the chemical activity of the hydrogen liberated at the surface of a given metal, we must first remember that here, again, as in the reduction of sulfur derivatives, the activity indexes cover a very wide range, and that the metals follow nearly the same order in point of hydrogen activity, as may be seen from inspection of the last line with those above it. In every case Mg and Zn, on the one hand, and Co and Ni, on the other, are the extremes in the metal series, when arranged in order of increasing hydrogen activity.

In reducing the organic compounds we rechecked the influence of the degree of acidity upon the reduction process and determined the influence of alkalinity upon the process. The results of our study of this problem are given in Table 2.

TABLE 2

No.	Substance reduced	Normality of HCl	Zn, weight	Normality of NaOH	AlNi, weight
1	Methyl red	4	1.97	0.8	0.37
2		3	1.3	0.4	0.32
3		2	0.8	0.2	0.3
4		1	0.6	0.1	0.28

The data cited (Table 2) show that the lower the acidity or the alkalinity, the smaller the weight of metal required for reduction, and, hence, the closer the reaction solution approaches the neutral, the better the reduction by nascent hydrogen.

We also made a study of the behavior of some alloys, mostly prepared with aluminum as a base, in order to be able to perform reduction in either an alkaline or an acid medium. These alloys contained up to 10% of the second component. The second components included those that were acid-soluble, such as Co and Ni, and the acid-insoluble ones, such as Cu, Ag, Sb and Ta. We also prepared alloys based on zinc and containing 6% of cadmium.

TABLE 3

No.	Substance reduced	Al	AlAg	AlNi	AlCu	AlCo	AlTa	AlSb	Zn	ZnCd
1	Methyl red + HCl	0.19	1.9	0.1	0.35	–	–	0.2	1.0	0.17
2	Methylene blue + HCl	0.12	0.4	0.1	0.22	–	0.12	0.13	1.5	0.43
3	Methyl red + NaOH	0.2	0.34	0.05	0.3	0.1	0.18	0.2	–	–
4	$KMnO_4$ + NaOH	0.18	0.28	0.06	0.2	0.08	0.14	0.2	–	–

We explored the behavior of these alloys in reducing methyl red and methylene blue in an acid medium and in reducing methyl red and $KMnO_4$ in an alkaline medium, using the experimental procedure outlined above. In Table 3, which gives the test results, all the numerical values represent the grams of alloy required for reducing a standard volume of a solution of the substance to be reduced. These weights identify the alloys completely: the lower the weight, the more active the hydrogen displaced from the acid or the alkali.

In these tests the following quantities were used: 450 ml of a saturated solution of methyl red + 50 ml of HCl (1:1); 450 ml of a methylene blue solution with a concentration of 1.8 g per liter + 50 ml of HCl (1:1); 30 ml of a saturated solution of methyl red + 10 ml of a 2N NaOH solution; and 200 ml of a 0.001N $KMnO_4$ solution + 40 ml of a 2N NaOH solution.

Inspection of the table shows that Cu and Ag lower the hydrogen activity in every case, this being particularly true of Ag. Decolorizing a methyl red solution in an acid medium requires 0.19 g of aluminum, but 1.9 g, or 10 times as much, of the aluminum-silver alloy.

Similar instances have been reported in electrochemistry [2]. When even small traces of Cu, Ag, or Pt are added to a metallic cathode at which reduction takes place satisfactorily, the cathode's reducing ability drops almost to zero.

In contrast to Cu and Ag, such metals as Co and, especially, Ni activate hydrogen, as might have been expected from the data in Table 1. The third series of tests in Table 3 shows that 0.2 g of Al but only 0.05 g of its alloy with Ni is required for the reduction of methyl red in an alkaline medium, i.e., the activity of the hydrogen is increased fourfold, which is not without interest for chemical practice.

Thus, the hydrogen evolved at the surface of the nobler component of an alloy is transformed by contact action, the activity of the hydrogen being raised or lowered, according to our findings, as much as tenfold in one direction and fourfold in the other in aluminum alloys.

In our subsequent more detailed research into the effect of the second component upon hydrogen activity, we found it advisable to replace alloys, which were fairly hard to prepare at times, since the melting points of some components are as high as 3000°, by deposits of one metal upon the other by means of displacing the first metal from a solution of its salt, thus achieving the same goal as in alloys: the intimate contact between the two metals. This is effected technically as follows: 1 ml of a 1% solution of a salt of the nobler metal was poured into a flask containing powdered Zn or Al, and then the solution was slightly acidulated and agitated, after which it was removed and replaced by a hot solution consisting of 100 ml of a saturated solution of methyl red and 100 ml of 2N hydrochloric acid. If subsequent heating did not produce complete decolorization, the amount of metal used was increased in the next run, and vice versa. This method was used to establish the influence of the following metals upon the activity of hydrogen: Ag, Au, Cd, Hg, Pb, Sb, Bi, Pt, and Pd.

Table 4 gives the results of these tests, the first column giving the amount of pure Zn and Al required for the reduction of the methyl red, for the sake of comparison, while the other columns give the weights of the same two metals in contact with another component.

TABLE 4

Zn	ZnAg	ZnAu	ZnCd	ZnHg	ZnPb	ZnSb	ZnBi	ZnPt	ZnPd
2	2.6	3.6	0.4	0.3	0.5	0.5	1.2	0.12	0.035
Al	AlAg	AlAu	AlCd	AlHg	AlPb	AlSb	AlBi	AlPt	AlPd
0.05	–	0.16	–	0.04	0.024	0.015	0.02	0.01	0.01

These findings clearly disclose the following behavior pattern: when the second component is at the left of Zn or Al in D. I. Mendeleev's periodic system of the elements, more of these two elements by weight is required to reduce methyl red, and, conversely, the greater the precedence of the group to which the second element belongs, the less of these two elements is required. This is very clearly seen in the tests run with Zn in contact with Au and Pd. In contact with Au 3.6 g of zinc is required instead of the 2 g of the pure metal, i.e., nearly twice as much, whereas only 0.035 g of Zn is needed when in contact with Pd, or 1/60th as much.

It is worthy of note that when $AuCl_3$ is added to the Zn with the Pd deposited upon it in order to deposit Au as well, the activating effect of the palladium is gradually paralyzed as more and more of the $AuCl_3$ is added, being completely paralyzed when the amount of $AuCl_3$ added is 20 times that of the $PdCl_2$; this agrees with the action of each of these metals upon hydrogen. Here, therefore, we see the antagonism of two components acting in opposite directions.

A study of the behavior of a large number of insoluble metals raises the question of whether the phenomenon of periodicity in the changes of hydrogen activity, set forth prudently in our first report, also applies to metals. This theoretical side of the problem was the second objective of our investigation of alloys and contact agents. In solving this problem it is advisable to make use of Table 2 in our first report, in which the metals are arranged according to the increasing activity of the hydrogen liberated at their surfaces in each row of D. I. Mendeleev's periodic table, and to expand it to include the insoluble metals, in view of the fact that if Ag and Au lower the activity of the hydrogen displaced from an acid by zinc, even though only slightly, this entitles us to place them in the table one group to the left, while, conversely, the increase in the activity of the hydrogen displaced by aluminum, due to additions of Pb, Sb, Bi, Pt, and Pd, justifies the latter elements being placed to the right of

aluminum, i.e., in the senior groups of the table. Hence, the arrangement of the soluble metals in the table is based upon the numerical indexes of the hydrogen activity, which are indicated above the symbols for the metals. The insoluble metals are located according to whether they lower or raise the activity of the hydrogen displaced by zinc and aluminum (Table 5).

TABLE 5

Row	Group of elements							
	I	II	III	IV	V	VI	VII	VIII
III		0.5 Mg	12 Al					
IV							35 Mn	50 Fe 80 Co 125 Ni
V		5 Zn						
VI								Pd
VII	Ag	7 Cd		14 Sn	Sb			
VIII								Pt
IX	Au	Hg		Pb	Bi			

As we see, the order in which the metals are arranged according to hydrogen activity is in no way different from their arrangement in D. I. Mendeleev's periodic table. Inasmuch as the number of metals investigated has nearly doubled, while we still observe no perceptible deviations from the general pattern of behavior, namely, that in each row of the table the hydrogen activity increases with the number of the group, we may conclude that the experiments described have not only confirmed the periodicity phenomenon, but have also extended it to the insoluble metals.

In the light of all that has been said about the periodic change in the activity of nascent hydrogen, such well-known facts as the high chemical activity of hydrogen in the presence of metals of Group VIII, such as Ni, Pt, and Pd, become quite understandable, and it is a matter of some regret that the phenomenon of periodicity in the catalytic action of metals upon hydrogen was not observed earlier, though reasons therefore existed, namely, that the strongest hydrogenation catalysts were all in the same group (VIII), which could only be due to periodicity.

The phenomena of periodicity manifested in the catalytic action of metals upon hydrogen gives us grounds to suspect that the phenomenon of periodicity may obtain in other catalytic reactions affected by catalysts of similar composition, such as oxides of various metals, sulfides, various cations, and the like.

In conclusion, it should be pointed out that although the activity of nascent hydrogen may be extremely high at times, there is no reason to exaggerate it, and this hydrogen may compete as a reducing agent only in rare cases with such energetic reducers as $Sn^{\cdot\cdot}$, $Cr^{\cdot\cdot}$, $Tl^{\cdot\cdot\cdot}$, and $V^{\cdot\cdot\cdot}$, as is proved by the fact that a methyl red solution is decolorized at a moderate rate in the presence of Ni dissolving in an acid, whereas all we have to do to cause this decolorization to take place almost instantaneously is to throw a grain of chromium, tin, ferrotitanium, or ferrovanadium into the solution. Only the presence of disperse Pt or Pd renders the hydrogen active enough to compete as a reducing agent with the foregoing ions. This is allowed for in the recent literature, the reduction of nitrobenzene in the presence of Sn and HCl being attributed to $Sn^{\cdot\cdot}$ rather than to hydrogen.

V. A. Kustodina rendered great technical assistance in the completion of this section of the research.

SUMMARY

1. The differences in the chemical activity of the hydrogen evolved at various metals have been confirmed by reducing a number of new objects: methyl red, methylene blue, pyronine, indigo carmine, and permanganate, it having been found that the differences are as great as they were in the reduction of sulfur derivatives.

2. The conclusion regarding the periodicity obtaining in the change of the activity of nascent hydrogen made in our first report has been confirmed by a study of the effect of various acid-insoluble metals upon hydrogen: Ag, Au, Hg, Pb, Sb, Bi, Pt, and Pd.

3. In a study of alloys and contact agents of two metals it has been found that the second component may lower the hydrogen activity tenfold (as in Ag) or increase it 60 times (as in Pd).

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SOLUBILITY EQUILIBRIA IN THE $K_2Cr_2O_7 - K_2SO_4 - H_2O$ SYSTEM

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Research into the equilibria in the $K_2Cr_2O_7 - K_2SO_4 - H_2O$ system represents a continuation of our comparative study of the mutual solubility of salts in simple ternary aqueous systems that contain potassium as the common ion and potassium dichromate as the common salt component [1].

The findings on the mutual solubility of potassium bichromate and sulfate are of practical importance in dichromate technology, inasmuch as the aqueous system consisting of these salts is a part of the reciprocal $Na_2Cr_2O_7 + K_2SO_4 \rightleftarrows K_2Cr_2O_7 + Na_2SO_4$ system, often employed in preparing potassium dichromate from sodium dichromate. This aqueous system of salts is also produced in the conversion of a chromate into a dichromate in the reaction $2K_2CrO_4 + H_2SO_4 \rightleftharpoons K_2Cr_2O_7 + K_2SO_4 + H_2O$, which is ordinarily used in the final stage of the technological process to prepare dichromate from chrome iron ore.

In so far as we have been able to gather from the literature, the $K_2Cr_2O_7 - K_2SO_4 - H_2O$ system has not been investigated at all. We have secured experimental data for the following solubility isotherms: 20, 25, 30 and 40°, for this system by the procedures usually employed in the isothermal method.

The composition of the liquid phase was established by determining the SO_4'' and Cr_2O_7'' quantitatively. These determinations were used to calculate the percentages of $K_2Cr_2O_7$ and K_2SO_4 in the analyzed sample of the liquid phase. The SO_4'' was determined gravimetrically, while the Cr_2O_7'' was determined by iodometric titration. The experiments used to determine the given composition were repeated, as a rule. The composition at the isothermal invariant points is the mean value of numerous determinations, the results of the various analyses exhibiting good coincidence.

The composition of the solid phase in equilibrium with the solution was determined chiefly by observing the appearance of a bottom sample under the microscope. In the microscope's field the triclinic colored crystals of potassium dichromate are sharply distinct from the colorless crystals of potassium sulfate. In monovariant isothermal curves the solid phases are individual salts, while at the isothermal invariant points they are mixtures of salts. All the data on our research into the $K_2Cr_2O_7 - K_2SO_4 - H_2O$ system are collected in Table 1 and plotted graphically in Fig. 1.

In describing the effect of other salts upon the solubility of any given salt, it is best to employ the comparative analysis of mutual solubility in a series of ternary aqueous salt systems.

We made this comparison, based on the mutual solubility at 20°, for the following systems: $K_2Cr_2O_7 - KCl - H_2O$ [2], $K_2Cr_2O_7 - KBr - H_2O$ [1], $K_2Cr_2O_7 - KNO_3 - H_2O$ [2], $K_2Cr_2O_7 - K_2SO_4 - H_2O$.

The solubility equilibrium diagrams are simple ones in these systems. The composition of the solutions is governed by the ions that make up the crystalline structures of the salts. All the systems have the same cation and a common salt component. The differing ions are all anions.

In this instance, the problem may be reduced to a comparison of the monovariant crystallization curves of potassium dichromate with the respective solubility isotherms.

This comparison is based upon the following assumptions.

1. In a three-component system, a solution that is not saturated with one of the components may be regarded as a new solvent with respect to the component with which the solution is saturated [3]. Hence, the monovariant isothermal curves can describe the solubility of the saturated salt solution in the presence of varying amounts of the other salt.

2. Dissolution and crystallization depend upon the singularities of the crystalline structure of a salt,

TABLE 1

Point No.	Per cent by weight			Molecular per cent			Solid phase
	H_2O	$K_2Cr_2O_7$	K_2SO_4	H_2O	$K_2Cr_2O_7$	K_2SO_4	
				20° Isotherm			
1	88.9	11.1	–	99.24	0.76	–	
2	88.82	10.16	1.02	99.19	0.69	0.12	
3	88.69	9.91	1.40	99.16	0.68	0.16	
4	88.60	9.53	1.87	99.13	0.65	0.22	K_2Cr_2O
5	88.06	8.56	3.38	99.02	0.59	0.39	
6	87.78	7.80	4.42	98.95	0.53	0.52	
7	86.67	6.92	6.41	98.76	0.48	0.76	
8	85.53	6.24	8.23	98.58	0.44	0.98	$K_2Cr_2O_7 + K_2SO_4$
9	86.10	5.42	8.48	98.62	0.34	1.00	
10	86.91	4.20	8.89	98.67	0.29	1.04	
11	87.49	3.08	9.43	98.69	0.21	1.10	K_2SO_4
12	88.38	1.98	9.64	98.77	0.11	1.12	
13	89.65	0.45	9.90	98.85	0.03	1.13	
14	90.0	–	10.0	98.87	–	1.13	
				25° Isotherm			
1	86.92	13.08	–	99.08	0.92	–	
2	86.35	12.09	1.56	98.97	0.85	0.18	
3	85.91	11.14	2.95	98.86	0.79	0.35	
4	85.73	10.12	4.15	98.79	0.71	0.50	$K_2Cr_2O_7$
5	85.05	9.15	5.80	98.65	0.65	0.70	
6	84.29	7.70	8.01	98.48	0.55	0.97	
7	84.24	7.43	8.33	98.46	0.53	1.01	$K_2Cr_2O_7 + K_2SO_4$
8	84.66	6.69	8.65	98.48	0.48	1.04	
9	85.05	6.15	8.80	98.51	0.44	1.05	
10	86.37	4.03	9.60	98.59	0.28	1.13	
11	86.95	3.13	9.92	98.62	0.22	1.16	
12	87.62	2.28	10.10	98.65	0.17	1.18	K_2SO_4
13	88.31	1.19	10.50	98.70	0.09	1.21	
14	88.56	0.74	10.70	98.72	0.05	1.23	
15	89.20	–	10.80	98.76	–	1.24	
				30° Isotherm			
1	84.6	15.4	–	98.90	1.10	–	
2	83.98	13.16	2.86	98.70	0.95	0.35	
3	83.14	12.20	4.66	98.54	0.89	0.57	
4	82.66	11.39	5.95	98.44	0.83	0.73	$K_2Cr_2O_7$
5	82.10	10.15	7.75	98.30	0.74	0.96	
6	81.59	9.75	8.66	98.20	0.72	1.08	
7	81.52	9.41	9.07	98.18	0.69	1.13	$K_2Cr_2O_7 + K_2SO_4$
8.	83.45	6.80	9.75	98.32	0.49	1.19	
9	85.31	4.54	10.15	98.47	0.32	1.21	
10	86.12	3.48	10.40	98.53	0.24	1.23	
11	86.32	2.94	10.74	98.52	0.21	1.27	
12	87.09	1.76	11.15	98.57	0.12	1.31	K_2SO_4
13	87.71	1.01	11.28	98.62	0.07	1.31	
14	88.52	–	11.48	98.68	–	1.32	
				40° Isotherm			
1	79.4	20.6	–	98.44	1.56	–	$K_2Cr_2O_7$

TABLE 1 - (continued)

Point No.	Per cent by weight			Molecular per cent			Solid phase
	H_2O	$K_2Cr_2O_7$	K_2SO_4	H_2O	$K_2Cr_2O_7$	K_2SO_4	
			40° Isotherm				
2	79.38	19.45	1.17	98.37	1.48	0.15	
3	79.36	18.94	1.80	98.33	1.44	0.23	
4	78.81	17.65	3.54	98.20	1.35	0.45	
5	78.71	16.89	4.40	98.14	1.29	0.57	$K_2Cr_2O_7$
6	78.49	15.98	5.53	98.07	1.22	0.71	
7	78.13	15.24	6.63	97.97	1.17	0.86	
8	77.63	14.61	7.76	97.86	1.13	1.01	
9	77.40	14.40	8.20	97.81	1.12	1.07	$K_2Cr_2O_7 + K_2SO_4$
10	79.46	11.66	8.88	97.99	0.88	1.13	
11	80.50	9.90	9.60	98.05	0.74	1.21	
12	81.65	8.30	10.05	98.14	0.61	1.25	
13	82.68	6.88	10.44	98.22	0.50	1.28	
14	83.60	5.60	10.80	98.29	0.40	1.31	
15	84.02	4.45	11.43	98.30	0.32	1.38	
16	84.44	3.71	11.85	98.31	0.26	1.43	K_2SO_4
17	85.10	2.70	12.20	98.35	0.19	1.46	
18	85.18	2.46	12.36	98.35	0.17	1.48	
19	85.70	1.84	12.46	98.39	0.13	1.48	
20	85.90	1.34	12.76	98.36	0.13	1.51	
21	86.72	0.34	12.94	98.46	0.02	1.52	
22	86.9	–	13.1	98.47	–	1.53	

which are governed by the fundamental nature and type of the chemical bond within the crystals for every solid [4]. Therefore, under the given thermodynamical conditions, the formation of solid phases in heterogeneous systems is largely governed by the available possibilities in the field of the chemical bond that can be actually realized in the formation of a stable crystalline structure. From the energy standpoint, this process is generally characterized by such interaction among the crystal's structural units (ions, atoms, and molecules) as will result in the system having a minimum energy.

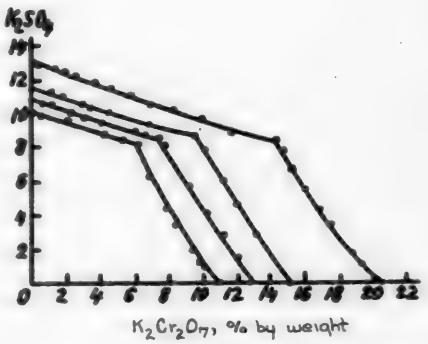

Figure 1

3. The process of crystallization of a salt from a dilute ternary solution by isothermal evaporation, as well as the establishment of a state of equilibrium by the addition of another salt to a saturated solution of the given salt, are best related to a given value of the solution's ionic strength. In the comparative evaluation of mutual solubility, the ionic strength gives a fuller characterization of such a property as, say the solubility of a given salt in the presence of other salts than the solution concentration does, since using the ionic strength makes it possible to relate the change in solubility of the given salt in various ternary systems to the change in the solution structure due to the substitution of one noncommon ion for another.

Figure 2 is a general diagram of the solubility isotherms at 20° for the four systems specified above.

We see from this diagram that the crystallization branches for potassium dichromate in the $K_2Cr_2O_7 - KBr - H_2O$ and $K_2Cr_2O_7 - KCl - H_2O$ systems, which contain substances that are similar from the standpoint of crystal chemistry as the second salt components, are of the same type. These branches determine the

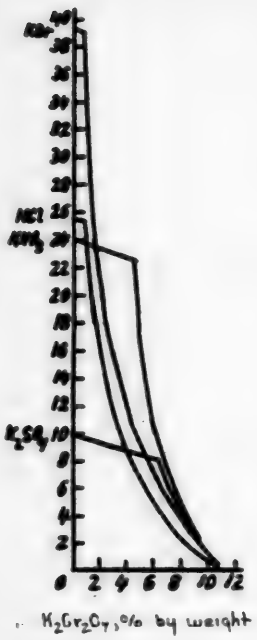

Figure 2.

nature of the equilibria prevailing in both systems, whereas the crystallization branches for the KBr and KCl are of practically no importance, inasmuch as the solubilities of these salts in isothermally invariant solutions are practically the same as their individual solubilities. Hence, it may be stated that in the ternary solutions used for comparison, containing the spherical Cl' or Br' anions as the noncommon ions in combination with the complex Cr_2O_7'' anion, the structural and energy conditions are such as to lower the individual solubility of the salt component with the more complicrystal structure considerably. Moreover, aqueous solutions of such substances as KCl and KBr may be regarded as equivalent aqueous salt solvents for potassium dichromate.

The salt series KCl (KBr), KNO_3, K_2SO_4, and $K_2Cr_2O_7$, which are the constituents of the systems under comparison, exhibits a comparative complication of crystal structure. As we have stated above, the first two salts are crystallochemically alike. Their isomorphism, in the narrow sense of the term, is a matter of common knowledge. The last three salts differ from the first two, as well as differing from one another, in point of the structural data pertaining to the complex anions, since in such salts as KNO_3, K_2SO_4, and $K_2Cr_2O_7$, structure is largely determined by the form and dimensions of the complex anion, which, in turn, depend upon the nature of the chemical bond and the coordination between the cation and the anion within the coordinated group.

Therefore, the noncommon anions in our ternary systems have structures of varying complexity: Cl' and Br' are spherical anions; NO_3' is triangular; SO_4'' is tetrahedral; the structure of Cr_2O_7'' is not yet definitely established, though this anion is apparently one of the pyro-ions of the S_2O_7'' type, with the general shape of $O_nA-O-AO_m$ [5].

Pursuing the comparison of the cited solubility isotherms on a crystallochemical basis, we may set down the general conclusion that as the crystal structure of the second salt components grows more complicated, the solubility of the potassium dichromate in the respective ternary systems increases.

Comparison of the monovariant curves for potassium dichromate in the $K_2Cr_2O_7-KCl-H_2O$ and $K_2Cr_2O_7-KNO_3-H_2O$ systems indicates a substantial increase in the solubility of the potassium dichromate when the NO_3' and Cr_2O_7'' ions are combined in ternary solutions. We see from this comparison that the range of concentrations of potassium nitrate solutions in which potassium dichromate can be dissolved is more restricted than in the $K_2Cr_2O_7-KCl-H_2O$ system, notwithstanding the fact that the individual solubilities of KCl and KNO_3 are not very far apart.

The diagrams likewise show that in ternary solutions in which the concentrations of the second salt component are alike the potassium dichromate is more soluble in solutions that contain potassium nitrate.

There is no doubt that these experimental data may be interpreted so that the change in the structure and energy of potassium dichromate in the $K_2Cr_2O_7-KNO_3-H_2O$ system, relative to the $K_2Cr_2O_7-KCl-H_2O$ system, depends largely upon the structure of the NO_3' ion: its form, dimensions and charge.

The combination of such large and structurally complicated anions as SO_4'' and Cr_2O_7'' in the ternary solutions of the $K_2Cr_2O_7-K_2SO_4-H_2O$ system is less favorable for the crystallization of potassium dichromate, so that the solubility of this salt is higher than in the systems considered previously. Potassium sulfate exhibits only slight salting-out action with respect to potassium dichromate, and both salts crystallize out together when the concentration of potassium sulfate is only slightly higher in the isothermal invariant solution. The combined action of the two salts diminishes their nearly similar individual solubilities to values that are not very far from, say, those in the $K_2Cr_2O_7-KCl-H_2O$ system.

As we have stated above, we combined a study of a property such as the solubility of a given salt in solutions containing varying compositions of other salts with an allowance for the ionic strengths of the solutions at which the salts crystallized. Let us assume that we have a solution of the $K_2Cr_2O_7-KBr-H_2O$

system that is dilute with respect to both of the salts, with a given value of ionic strength and a definite ratio of the ionic strengths of the salts making up the system. Say, this ratio is unity, for example. When such a solution is evaporated isothermally, the points representing its composition will all lie on a straight line connecting the water vertex of the diagram to a certain point on the monovariant crystallization curve for potassum dichromate (Figure 3). The transition from a solution that is unsaturated with respect to one salt to a saturated solution involves the establishment of a solid phase. This phase formation occurs at a certain value of the solution's ionic strength, the given ratio between the summand values of the salts' ionic strengths remaining unchanged.

In the 20° isotherm we have reproduced, the potassium dichromate crystallizes all the way up to the isothermal invariant point throughout a wide range of values for the ratio of the ionic strength of the saturating salt's solution to the

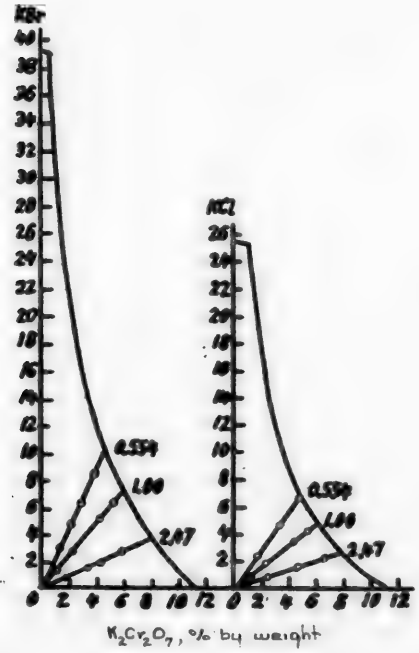

Figure 3

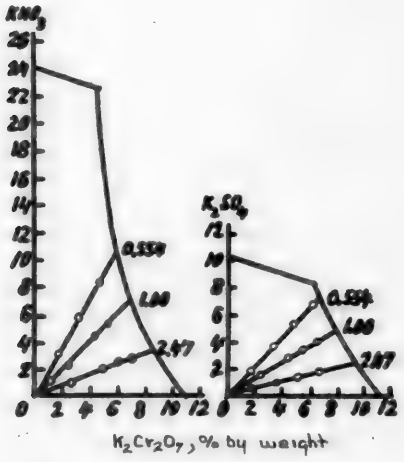

Figure 4

ionic strength of the nonsaturating salt's solution, the overall ionic strength of the solution increasing uninterruptedly. We see from the composition of the isothermal invariant solution that increasing the concentration of potassium bromide in the ternary solutions results in the nearly complete salting-out of the potassium dichromate. Hence, the interaction between ions and between ions and molecules of the solvent in ternary solutions of the $K_2Cr_2O_7 - KBr - H_2O$ system is such as to cause almost total replacement of the potassium dichromate by the potassium bromide. It is useful to describe such interaction between particles in solution as regards such a property as the solubility of the freely soluble salt in various water-salt solvents by definite values of the ionic strength, even if only in the most general manner.

Figures 3 and 4 are diagrams of the 20° isotherms for the four solutions under comparison, with three rays representing the following ratios of the ionic strength of the potassium dichromate to the ionic strength of the respective other salt: 3.47; 1; and 0.554. The underlying numerical figures for these diagrams are listed in Table 2.

The ratio of the ionic strengths of the salts is denoted by the letter a in the table. The solution ionic strengths were calculation from the equation:

$$\mu = \frac{1}{2}\,(m_1 z_1^2 + m_2 z_2^2 + \ldots)$$

TABLE 2

Value of a	Grams per 100 g of saturated solution		Solution ionic Strength	Solid phase	Grams per 100 g of saturated solution		Solution ionic Strength	Solid phase
	$K_2Cr_2O_7$	KBr			$K_2Cr_2O_7$	KCl		
	$K_2Cr_2O_7 - KBr - H_2O$				$K_2Cr_2O_7 - KCl - H_2O$			
2.47	8.06	3.96	1.312	$K_2Cr_2O_7$	7.99	2.46	1.279	$K_2Cr_2O_7$
1.00	6.00	7.28	1.411		6.17	4.69	1.411	
0.554	4.53	9.92	1.514		4.80	6.60	1.551	
	$K_2Cr_2O_7$	KNO_3			$K_2Cr_2O_7$	K_2SO_4		
	$K_2Cr_2O_7 - KNO_3 - H_2O$				$K_2Cr_2O_7 - K_2SO_4 - H_2O$			
2.47	8.49	3.54	1.383	$K_2Cr_2O_7$	9.41	2.26	1.521	$K_2Cr_2O_7$
1.00	6.85	7.05	1.621		7.90	4.70	1.847	
0.554	5.90	10.97	2.03		6.56	7.01	2.169	

where μ is the ionic strength, m is the molarity, and z is the charge on the ion [6].

We see from the table that at certain values of a the crystallization of potassium dichromate occurs at practically identical values of the solution ionic strength in the $K_2Cr_2O_7 - KBr - H_2O$ and $K_2Cr_2O_7 - KCl - H_2O$ systems. The potassium dichromate crystallizes at other, higher values of ionic strength in the two systems $K_2Cr_2O_7 - KNO_3 - H_2O$ and $K_2Cr_2O_7 - K_2SO_4 - H_2O$ at the same values of a.

This brief analysis of the experimental findings on the mutual solubility of salts enables us to estimate the presence of equivalent water-salt solvents for a given salt by means of its structural similarity to the respective salts. It might also be stressed that various instances of change in the individual solubilities of salts in ternary water-salt systems are definitely affected by the crystallochemical structurall features of the salt components.

SUMMARY

1. Solubility in the $K_2Cr_2O_7 - K_2SO_4 - H_2O$ system has been investigated at 20, 25, 30 and 40° by the methods of physicochemical analysis.

2. It has been shown that it is possible to systematize the experimental data on mutual solubility in ternary water-salt systems by allowing for the crystallochemical structural data of the salts.

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THE KINETICS OF CINNAMIC ACID HYDROGENATION

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The rate of catalytic hydrogenation of a dissolved substance that is continuously agitated with a finely pulverized catalyst in a current or an atmosphere of nitrogen by the method first employed by Fokin [1], depends upon the temperature, the concentration of the solute, the nature of the solvent, the hydrogen pressure in the gas phase, the nature of the bond to be hydrogenated, the presence of other efficiently adsorbing groups in the molecule, the degree of substitution of the bond to be hydrogenated (the screening), the quantity of catalyst, the activity and the nature of the catalyst, and the rate of stirring (number of oscillations). An equation has recently been derived for the velocity of hydrogenation that allows for the existence of a semihydrogenated state at the surface and for two kinds of surface – one activating the substance to be hydrogenated and the other activating the hydrogen.

Of the factors listed above, the following determine the operational procedure: temperature, hydrogen pressure, solute concentration, nature of the solvent, quantity of the catalyst, activity and nature of the catalyst, and rate of stirring. There are only scattered papers dealing with the interrelated study of all or at any rate most of the kinetic factors specified. Most papers deal with an investigation of the effect of a single factor, most frequently the nature of the catalyst.

The rate of catalytic hydrogenation in the liquid phase may be described by equations ranging from zero order to the second order, depending upon the process conditions, the nature of the substance undergoing hydrogenation, and the nature of the catalyst. We often come across fractional orders, as well as instances of the order of reaction changing in the course of the process.

Many of the authors of papers on catalytic hydrogenation in the liquid phase have not paid enough attention to the need for making a distinction between the "diffusion" and the "kinetic" regions in the hydrogenation process. In the diffusion region, the hydrogenation velocity is governed by the rate of diffusion of the initial substances, the unsaturated compound and the hydrogen, toward the catalyst's surface or of the reaction products into the solution. In the kinetic region one of the processes occurring directly at the surface is the stage that limits the overall velocity. Whether a given process takes place in the kinetic or the diffusion region is determined by the process conditions: temperature, pressure, stirring rate, and quantity of catalyst [2, 3]. At least 250-300 oscillations of the hydrogenation apparatus must be ensured for the hydrogenation reaction to take place in the "kinetic" region.

Elovich and Zhabrova [4] have made a detailed study of how the stirring rate affects the kinetics of hydrogenating styrene in glacial acetic acid over $Pt/BaSO_4$.

Our research has dealt with a study of the kinetics of hydrogenation over a nickel catalyst prepared by leaching out a 50% nickel–aluminum alloy with lime and called "skeletonized nickel". We used apparatus of our own design, with precise temperature control and very intensive stirring [3, 5].

OPERATIONAL PROCEDURE

The major parts of the installation were the gas buret, fitted with a water jacket to keep the temperature constant, and the hydrogenation device proper – the "duck". The duck was attached to holes in a coupling and was brought into strong and regular motion by a 0.25 kw motor; the oscillations of the duck could be varied from 200 to 1600 per minute. The oscillation length was variable, but it was 5.2 cm as a rule. The number of oscillations was checked by measuring the rpm. The duck was oscillated in a water thermostat (0.1 m^3), fitted with a stirrer and a thermoregulator. The variation of temperature within the thermostat did not exceed $\pm$ 0.1°. The duck was immersed in the thermostat up to its stopcock, so that all its contents were beneath the level of the water. The size of the apparatus enabled us to attach two ducks to the coupling at the same time, thus running parallel tests.

A three-way stopcock was used to connect the gas buret either to a gasometer containing hydrogen or to the duck. Water was used as the sealing fluid in the buret. The hydrogen was produced by electrolyzing a 20% solution of NaOH, using platinum or nickel electrodes. The traces of oxygen were removed from the hydrogen in a furnace, using platinized asbestos or metallic copper, while the traces of sulfur compounds were removed by passing the hydrogen through an alkaline solution of plumbite.

A sample of the substance (from 0.1 to 0.2 g) was transferred to the duck by means of a solvent, a weighed amount of the catalyst was added, and then some more of the solvent.[1]

Then the air was driven out of the system by passing large volumes of hydrogen (ranging from 0.5 to 1.0 liter) through it or by alternately pumping out the duck and filling it with hydrogen (testing the hydrogen for purity after evacuation).

The starting of the agitation motor was fixed as the start of the run, with the amount of hydrogen taken from the gas buret recorded against a stop watch. The runs lasted from 3 minutes to several hours. The end of hydrogenation was determined by the absence of any change in the water level within the buret during the course of several minutes.

The order in which the various constituents were introduced into the duck was varied, the exact order being stated in the text each time. Whenver catalysts or the substance to be hydrogenated were added during the course of the run, the motor was disconnected, the operation continuing in a current of hydrogen.

Cinnamic acid was chosen as the test substance. In our subsequent experiments cinnamic acid has served as a reference standard for comparing the hydrogenation rates of various organic compounds. Commerical cinnamic acid, recrystallized twice from distilled water, was dried at 105°; its m.p. was 132.5°.

The catalyst was prepared from an alloy containing 50% Ni and 50% Al.

After several tests, we settled upon the following procedure for preparing an activated catalyst: 1 g of the alloy, finely pulverized in a mortar, was placed in a flask fitted with a reflux condenser, which contained 80 ml of an NaOH solution that had been first heated on a boiling water bath. Leaching on the water bath lasted two hours, after which the alkali was decanted, and the catalyst was washed by decanting it four times with 100-ml portions of distilled water and twice with alcohol (20 ml). In this washing some of the light particles of the catalyst are lost, and its activity is diminished appreciably. To prevent loss, all the wash waters were poured into a single bottle, the small quantity of catalyst particles that settled with time being separated by another decantation and then combined with the bulk of the catalyst, the whole being transferred to the duck. It is even better to decant the bulk of the wash waters and then to centrifuge the remainder.

In one of our tests, the catalyst, consisting of 1 g of alloy, was washed with 400 ml of water and 20 ml of 95% alcohol, transferred to a U-shaped tube and dried in a current of hydrogen. The catalyst then weighed 0.565 g.

Experiment No. 1. 0.5 gram of cinnamic acid was dissolved in 15 ml of 95% alcohol and placed in a duck; the catalyst (0.56 g) was added, together with another 10 ml of alcohol. The air was driven out of the duck by hydrogen, and the motor was started as soon as the solution to be hydrogenated had reached the temperature of the thermostat. The thermostat temperature was 25° (±0.1°), the temperature of the water in the jacket of the measuring buret being 10°. The pressure (p) was 697.5 mm; the "duck" was oscillated back and forth 330 times per minute; and the length of the "duck" travel was 5.2 cm.

As this experiment shows, the reaction rate is satisfactorily described by an equation for a first-order reaction. The velocity constant, calculated graphically, was 0.051. Hydrogenation is complete, and a drop in the velocity constant is observed only after 65 ml of hydrogen (i.e., more than 3/4) had been absorbed. The velocity rate is very low when no stirring is used or when the number of oscillations is low; at upward of 300-330 duck oscillations per minute, however, the reaction rate at 25° is practically independent of any further increase in the stirring rate. This is indicated by the figures in Table 2.

The reaction remains a first-order one as the stirring rate is increased and the temperature is varied. This enables us to calculate the apparent activation energy of the hydrogenation of cinnamic acid in alcohol solution over skeletonized Ni. The activation energy, as calculated from the formula:

[1] The dimensions of the duck enabled us to vary the total liquid volume from 10 to 50 ml.

TABLE 1

Experiment 1

Time, Minutes	V_θ	$\frac{\Delta V_\theta}{\Delta t}$	$\frac{\Sigma V_\theta}{2}$	Time, Minutes	V_θ	$\frac{\Delta V_\theta}{\Delta t}$	$\frac{\Sigma V_\theta}{2}$
0	0.0	5.6	2.8	17	58.6	2.1	59.6
1	5.6	4.7	8.0	18	60.7	2.1	61.8
2	10.3	4.6	12.6	19	62.8	2.0	63.8
3	14.9	4.2	17.0	20	64.8	1.7	65.6
4	19.1	3.7	21.0	21	66.5	1.6	67.3
5	22.8	3.7	24.6	22	68.1	1.4	68.8
6	26.5	3.5	28.2	23	69.5	1.4	70.2
7	30.0	3.5	31.8	24	70.9	1.0	71.4
8	33.5	3.3	35.2	25	71.9	1.1	72.3
9	36.8	3.3	38.4	26	73.0	0.8	73.4
10	40.1	3.0	41.6	27	73.8	0.7	74.2
11	43.1	2.5	44.4	28	74.5	0.5	74.8
12	45.6	2.9	47.0	29	75.0	0.24	75.6
13	48.5	2.8	49.9	34	76.2	0.16	76.6
14	51.3	2.5	52.6	39	77.0	0.0	77.0
15	53.8	2.5	55.0	44	77.0	0.0	77.0
16	56.3	2.3	57.4	49	77.0	—	—

TABLE 2

Variation of the Rate of Hydrogenation of Cinnamic Acid with the Number of Duck Oscillations

Hydrogenation conditions: 0.5 g of cinnamic acid; 25 ml of 95% alcohol as the solvent; catalyst prepared from 1 g of 50% alloy.

Test No.	Temperature	Oscillations per minute (back and forth)	K
1 (7)	25°	330	0.051
2 (8)	25	440	0.044
3 (5)	25	550	0.048
4 (9)	25	650	0.047
	Average		0.0475
The same behavior pattern is repeated at 0°			
5 (11)	0	300	0.010
6 (12)	0	300	0.010
7 (13)	0	400	0.011
8 (10)	0	440	0.013
	Average. . . .		0.0115

TABLE 3

Variation of the Rate of Hydrogenation of Cinnamic Acid with the Volume of Solvent

Hydrogenation conditions: 0.5 g of cinnamic acid; catalyst prepared from 1 g of alloy

Test No.	Ml of alcohol	K
7	15	0.012
6	25	0.012
8	50	0.011

$$E = \frac{RT_1T_2}{T_2 - T_1} 2.3 \log \frac{K_2}{K_1} \sqrt{T_1/T_2}$$

was found to be 9108 ±1000 cal per mole.

It was found that the velocity constant remained the same when the concentration of cinnamic acid was varied (varying the volume of solvent from 15 to 50 ml), though keeping the catalyst quantity constant and keeping the rate of agitation constant at a sufficiently high level (Table 3).

We also investigated the variation of the rate of hydrogenation of cinnamic acid with the quantity of catalyst used, varying the latter from 1 to 4 g, based on the Ni-Al alloy. The catalyst was washed out, with the washings centrifuged. The respective data are to be found in Table 4.

It may therefore be regarded as certain that the hydrogenation rate is directly proportional to the quantity of catalyst (q) within the range investigated.

TABLE 4

Variation of the Rate of Hydrogenation of Cinnamic Acid with the Quantity of Catalyst Used (Based on the Alloy)

Hydrogenation conditions: 25 ml of 95% alcohol; 400 oscillations per minute; 0°; 0.5 g of cinnamic acid.

Test No.	Quantity of alloy	Method of leaching and washing	K	K/q
9	2.00	At once.....	0.038	0.019
6	1.00	At once.....	0.010	0.010
20	3.00	At once	0.056	0.019
11	2	In 1-g batches.....	0.022	0.011
12	1	With centrifuging...	0.010	0.010
21	4	In 2-g batches.....	0.072	0.018

Our method of preparing the catalyst yielded a rather active catalyst, with not unsatisfactory reproducibility of the tests; this was reinforced by the results of a special study on the variation of the activity of skeletonized Ni with the extent and duration of leaching. We leached out 1 g of the alloy on a boiling water bath for 5, 15, 30, 60, 75, 90, 120, 150, 180, 240, 360 minutes and more. Different quantities of hydrogen were evolved, corresponding to these intervals of time. As before, each catalyst sample was washed four times with distilled water and twice with alcohol. The results of these tests are listed in Table 5.

The catalyst was leached out for 6 hours

TABLE 5

Variation of the Activity of a Ni Catalyst with the Extent and Time of Leaching

Leaching conditions: 80 ml of 20% alkali; 1 g of alloy; temperature: boiling water bath. Hydrogenation conditions: 24°; 0.5 g of cinnamic acid; 25 ml of 95% alcohol as solvent; 400 oscillations per minute; oscillation length 5.2 cm; dimensions of duck — 3.7 X 14 cm.

Leaching time, minutes.....	5	15	30	60	75	90	120	150	180	240	360
Volume of hydrogen evolved during leaching out of the alloy, ml.....	375	415	500	660	675	715	715	715	715	715	715
Relative hydrogenation rate during the first five minutes	1.7	1.7	2.1	2.7	3.2	2.7	2.4	2.4	2.4	2.4	2.4

30 minutes on a boiling water bath and then allowed to stand in the alkali for 15 hours at room temperature.

We see that the activity of the catalyst remained unchaged after two hours of leaching, while the catalyst did not cake after prolonged heating at 100°. The production of maximum catalyst activity by leaching, as established in our research, supports the incomplete leaching of an Ni-Al alloy proposed by several authors [6].

It is therefore fully advisable to leach out the Ni-Al alloy partially in preparing a catalyst, after which it is activated by releaching as its activity falls off. Using this procedure, we can hydrogenate a substantial quantity of cinnamic acid without producing any perceptible change in catalyst activity; when pure hydrogen and cinnamic acid are employed, there is only little change in the activity of skeletonized Ni after 3 or 4 successive runs.

SUMMARY

1. A study has been made of the effect of stirring upon the kinetics of the hydrogenation of cinnamic acid dissolved in 96% ethyl alcohol over skeletonized Ni.

2. It has been found that cinnamic acid is hydrogenated in the "kinetic" region, the process being unaffected by any increase in the stirring rate over 300 oscillations of the duck per minute.

3. It has been found that the reaction is of the first order for cinnamic acid. The activation energy of the process has been found to be 9000 ± 1000 cal per mole.

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THE ELECTROCHEMICAL OXIDATION OF ANILINE IN THE PRESENCE OF CATALYSTS

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The assertion is made in various foreign patents [1] that aniline can be quantitatively oxidized to quinone electrochemically in solution when certain compounds are present.

In order to explore the effect of the presence of catalysts in the solution upon the electrochemical oxidation of aniline we ran a series of experiments on the electrochemical oxidation of sulfuric acid solutions of aniline with Mn, Cr, V, and Ce compounds, using platinum and lead electrodes.

We likewise investigated the kinetics of the anodic processes, using polarization curves.

EXPERIMENTAL

The apparatus used for electrolysis was set up in accordance with the layout usually employed for this purpose. The electrolyzer was a half-liter chemical glass beaker, inside which there was placed a 0.2-liter porous ceramic beaker. The glass beaker served as the cathode space. The ceramic beaker served as the anode space and as a diaphragm separating the cathode and anode spaces.

Cylindrical electrodes were used. The anode used was either a mesh made of 1-mm platinum wire, with a total surface of 13.5 cm^2, or a perforated lead plate, with a working surface of 200 cm^2. The cathode was a lead plate with a working surface of 280 cm^2.

The electrolyzer was connected in series with a coulometer and a milliammeter. The current source was a lead storage battery connected to a high-resistance rheostat. By means of the latter the required external voltage was taken from the storage battery and led to the electrolyzer. During electrolysis the anode potential was continuously checked, being kept within a certain range by regulating the external voltage. A saturated calomel electrode served as the reference electrode for measuring the anode potential. The electrode potential was measured by means of the customary compensation circuit, using a P-4 potentiometer.

When we plotted the polarization curves, we conducted electrolysis in the glass beaker without using the ceramic diaphragm. We used helical electrodes made of 1-mm platinum wire. The cathode was placed within a long glass tube 15 mm in diameter, set up vertically in the beaker with its lower edge 3-4 mm from the bottom of the beaker. In this setup intensive stirring with a mechanical stirrer was employed during electrolysis.

Analine, refined by double distillation with zinc dust, was employed in all our tests.

In electrolysis we used 0.3 molar (Pb anode) and 0.1 molar (Pt anode) solutions of aniline in 1.5-molar sulfuric acid containing compounds of one of the following elements: Mn, Cr, V, or Ce. Electrolysis was stopped after a certain quantity of electricity had passed through the solution, as determined by the coulometer.

A solid ranging in color from green to dark-green, plus some quinone, was produced in the anode space, depending upon the electrolysis conditions. The solid was separated from the liquid in a vacuum filter. The solution was extracted with ether. The ether was evaporated. The ether extract was combined with the solid residue and then distilled with steam. The percentage of quinone in the aqueous solution produced by steam distillation was determined iodometrically. The solid residue was thoroughly washed, first with soda and then with water, then separated from the liquid on a vacuum funnel, and dried at 100-110°. Its yield was determined by weighing. The dried product did not fuse at temperatures below 320°.

Experimental Results and Their Evaluation

The figure shows the polarization curves giving the current density as a function of the anode potential, plotted in the presence of Mn, Cr, V, and Ce compounds.

The anode potential, plotted as the abscissas, is the emf of the cell, consisting of the polarized electrode and the saturated calomel half-cell; it includes the potential jump at the liquid contact.

In all the cases we have investigated the polarization curve consisted of two branches. Under the conditions corresponding to the lower branch of the polarization curve nothing occurs during electrolysis but the oxidation of aniline at the anode. No oxygen or quinone is produced under these circumstances.

Under the electrolysis conditions corresponding to the upper branch of the polarization curve, the aniline is oxidized and oxygen is evolved, while a dark solid product is formed in the anodic region, together with a small amount of quinone.

Inspection of the polarization curves reproduced in the figure indicates that the presence of small amounts of Mn, Cr, V, or Ce has no appreciable effect upon the nature of the polarization curves, and, hence, upon the kinetics of the current-generating process.

The principal results of our experiments on the electrolysis of solutions of aniline in sulfuric acid with platinum and lead electrodes, as well as the experimental conditions employed, are given in Tables 1 and 2, respectively.

Polarization curves of aniline dissolved in sulfuric acid. 1) Without a catalyst; 2) Ce; 3) Cr; 4) V; 5) Mn.

Examination of the results listed in Tables 1 and 2 shows that small yields of quinone were secured in some instances when the aniline was oxidized. The quinone yield was higher when Mn, Cr, V, and Ce compounds were present (and a platinum electrode was used) than in the absence of these compounds. These elements differ somewhat in the degree to which they promote the yield of quinone.

TABLE 1

Electrolysis of Sulfuric Acid Solutions of Aniline with a Platinum Anode

Oxygen carrier	Anode potential, volts, referred to saturated calomel electrode	Amt. electricity passed through Ah	Yield of black aniline, g.	Yield of quinone, g.
None	2.0-2.2	4.3	1.12	0.026
$MnSO_4$ 0.067 m	1.7-2.1	3.15	1.8	0.21
	1.7-2.1	3.3	1.8	0.27
NH_4VO_3 0.067 m	2.1-2.5	2.1	–	0.03
	2.2-2.5	3.5	0.95	0.109
	2.1-2.5	4.1	0.88	0.084
$Cr(SO_4)_3$ 0.067 m	2.0-2.2	1.2	–	0.013
	2.0-2.2	4.1	–	0.084
CeO_2 0.067 m	2.35-2.50	4.3	1.09	0.167
	2.85-2.50	2.1	0.950	0.107
	2.35-2.50	4.8	–	0.164

TABLE 2

Electrolysis of Sulfuric Acid Solutions of Aniline with a Lead Anode

Oxygen carrier	Anode potential, volts, referred to saturated calomel electrode	Amt. electricity passed through Ah	Yield of black aniline, g.	Yield of quinone, g.
None	1.5	6.35	5.7	0
None	1.5-1.8	7.8	5.0	0
None	1.5	11.5	4.90	Traces
HVO_3 0.3 m	1.5-1.8	5.5	5.5	0
HVO_3 0.3 m	1.5-2.0	6.8	5.7	0.05
HVO_3 0.3 m	1.5-2.0	13.6	1.0	0.32
$MnSO_4$ 1.5 m . . .	1.5-2.0	5.8	4.3	0
$MnSO_4$ 1.5 m . . .	1.5-2.2	2.7	2.8	0
$Cr_2(SO_4)_3$ 1 m . .	1.5	8	4	0
$Cr_2(SO_4)_3$ 1.5 m ..	1.5-1.9	8	5.3	0

When a lead anode is used, quinone is formed only when vanadium compounds are present.

SUMMARY

A series of experiments has been run on the electrochemical oxidation of solutions of aniline in sulfuric acid containing compounds of Mn, Cr, V, and Ce, and it has been shown that these compounds increase the yield of quinone.

LITERATURE CITED

[1] German Patents 109012 (1897); 117129 (1899); 172654 (1903); 152063 (1903).

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THE PRODUCTION OF ORTHOTITANIC ACID ESTERS BY THE RE-ESTERIFICATION METHOD

E. A. Arbuzov and Z. G. Isaeva

Bischoff and Adkins [1] were the first to produce orthotitanic acid esters in the pure state, by reacting titanium tetrachloride with alcoholates. They secured a 67% yield of the tetraethyl ester, and 80% yields of the isopropyl and tetrabutyl esters.

They produced the tetramethyl ester by reacting tetraethyl orthotitanate with methanol. Tetraethyl orthotitanate has been produced by this method by other authors as well [2]. There are references in the patent literature to the production of titanium acid esters by the reaction of alcohols with titanium tetrachloride in the presence of nitrogen bases that bind the hydrogen chloride [3].

In our investigation of ortho acid esters by the method of dipole moments and parachors we found it necessary to synthesize esters of orthotitanic acid with the higher alcohols. In contrast to the patent data, we were unable to produce orthotitanic acid esters by reacting titanium tetrachloride with alcohols in the presence of dimethylaniline. Synthesis of orthotitanic acid esters by the action of alcoholates of the higher alcohols upon titanium tetrachloride is difficult, owing to the necessity of using large quantities of the higher alcohols to prepare alcoholate solutions, which led us to employ the re-esterification method to produce orthotitanic acid esters containing long alkyl radicals.

In producing the higher esters of orthotitanic acid, we used tetraethyl orthotitanate, which we succeeded in preparing from the alcoholate and titanium tetrachloride in absolute alcohol, the yield being 70% of the theoretical, provided the reagents were thoroughly protected against moisture.

The re-esterification of the ethyl ester with higher alcohols readily gave us high yields of the butyl, hexyl, octyl, and nonyl esters of orthotitanic acid as viscous liquids, faintly yellow in color, the constants of which were as follows:

TABLE

Ester	Yield, % of theoretical	B.p.	d_4^{20}	n_D^{20}
n-Butyl	76	166° (6.5 mm)	1.0051	1.4925
n-Hexyl	85.9	201-204 (2 mm)	0.9573	1.4830
n-Octyl	84.1	255-258 (2 mm)	0.9339	1.4810
n-Nonyl	77.9	264-265 (1.5 mm)	0.9241	1.4785

The hexyl, octyl, and nonyl esters have not been described previously in the literature.

After this research had been completed and the dipole moments of the synthesized esters had been measured [4], there appeared a paper by Speer [5], in which he describes the synthesis of several esters of orthotitanic acid by the action of titanium tetrachloride upon the alcoholates of the respective alcohols in benzene (the ethyl, n-propyl, n-butyl, isobutyl, sec-butyl, and n-octyl esters) and by a re-esterification reaction (tert-butyl ester). Like us, Speer was also unable to secure orthotitanic acid esters in the presence of nitrogen bases (dimethylaniline, pyridine, ammonia). The yields of orthotitanic esters secured by Speer were lower than those we secured by re-esterification.

EXPERIMENTAL

Synthesis of the butyl ester of orthotitanic acid. 10.6 g of the ethyl ester of orthotitanic acid, with a b.p. of 149-151° (11 mm), and 21 g (a 52% excess) of n-butyl alcohol were placed in an A. E. Arbuzov flask, and the flask was heated slowly. Ethyl alcohol was driven off, as was the excess of butyl alcohol in vacuo, and the residue was distilled. This yielded 10.2 g of orthobutyl titanate with a b.p. of 166° (6.5 mm), or 70% of the theoretical yield.

The orthotitanic acid ester was analyzed by saponifying a sample of the ester with water in a crucible at 30-35° and drying the resultant titanium oxide to constant weight in the flame of a soldering torch.

0.1314 g, 0.1144 g substance: 0.0314 g, 0.0268 g TiO_2. Found %: Ti 14.32, 14.04. $C_{16}H_{36}O_4Ti$. Calc.%: Ti 14.09.

Synthesis of the n-hexyl ester of orthotitanic acid. We used 6.5 g (0.028 mole) of the ethyl ester of orthotitanic acid and 11.6 g (0.113 mole) of hexyl alcohol in this reaction. The mixture was heated in an A.E.Arbuzov flask until no more ethyl alcohol was driven off. Distillation of the residue in vacuo yielded 9.8 g of the hexyl ester of orthotitanic acid, with a b.p. of 201-204° (2 mm), the yield being 85.9% of theoretical.

0.1304 g, 0.1000 g substance: 0.0222 g, 0.0174 g TiO_2. Found %: Ti 10.19, 10.43. $C_{24}H_{52}O_4Ti$. Calculated %: Ti 10.59.

Synthesis of the n-octyl ester of orthotitanic acid. We used 4.1 g of ethyl orthotitanate and 10.2 g of n-octyl alcohol. Driving off the ethyl alcohol and vacuum distillation yielded 8.5 g (84.1% of the theoretical yield) of octyl orthotitanate, with a b.p. of 255-258 g (2 mm).

0.1178 g, 0.1074 g substance: 0.0164 g, 0.0148 g TiO_2. Found %: Ti 8.35, 8.26. $C_{32}H_{68}O_4Ti$. Calculated %: Ti 8.49.

Synthesis of the n-nonyl ester of orthotitanic acid. We used 3.5 g ethyl orthotitanate and 10 g of n-nonyl alcohol. Driving off the ethyl alcohol and vacuum distillation yielded 7.4 g of a dark-red product, which turned light-yellow when allowed to stand for two days in a sealed ampoule. B.p. 264-265° (1.5 mm). Yield 77.9% of the theoretical.

0.1324 g, 0.1598 g substance: 0.0168 g, 0.0200 g TiO_2. Found %: Ti 7.61, 7.50. $C_{36}H_{76}O_4Ti$. Calculated %: Ti 7.73.

SUMMARY

High yields of the following esters of orthotitanic acid have been synthesized by the re-esterification of the ethyl ester of orthotitanic acid: the n-butyl, n-hexyl, n-octyl, and n-nonyl esters.

LITERATURE CITED

[1] Bischoff and Adkins. J. Am. Chem. Soc., 46, 256 (1924).

[2] Jennings, Wardlaw, and Way. J. Chem. Soc., 637 (1936); McCorquodale and Adkins, J. Am. Chem. Soc., 50, 1938 (1928); Gardner and Bielous. Chem. Abs., 25, 2971 (1931).

[3] British Patent 479470 (1938); Kraitzer, McTaggart, and Winter. Chem. Abs., 42, 1433 (1948).

[4] B. A. Arbuzov and T. G. Shavsha. Proc. USSR Acad. Sci., 68, 859 (1949).

[5] R. Speer. J. Org. Chem., 14, 655 (1949).

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THE RAMAN SPECTRA OF SOME TERPENE HYDROCARBONS

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The Raman spectra of many terpenes have been investigated more than once. When we compare the findings of various authors, however, we find great discrepancies, due to the preparations not being pure enough and to inaccuracies in frequency measurements. To be sure, satisfactory results may be obtained in the spectral analysis of products containing terpenes only if we have accurate and reliable data on the spectra of absolutely pure preparations of the individual compounds. The securing of such data is an indispensable step in achieving the effective spectral analysis of systems that contain complicated molecules, the spectra of which contain a very large number of lines.

The literature contains many papers on the spectroscopic investigation of mixtures of terpenes. Valuable data were secured in papers by Pigulevsky and others [1,2] on the composition of turpentine, which demonstrated that it was entirely possible to secure accurate spectra and to decipher them. The results of such investigations can be made even more complete provided we have accurate data on the spectra of the pure hydrocarbons.

We cite below the results of determinations of the Raman spectra of three terpenes: α-pinene, Δ^3-carene, and limonene, isolated in as pure a state as possible from pine turpentine. The spectra were photographed with a three-prism spectrograph equipped with glass optics with a linear dispersion of 27 Å/$\mu\mu$. The 4358.3 Å mercury line, separated by means of light filters, was used as the spectrum excitation. The spectra were recorded by photographing them on isochromatic photographic plates of average sensitivity. The slit width of the spectrograph was 5 cm^{-1}. The line frequencies were calculated by means of interpolation formulas, applying corrections determined from the standards of the iron-arc spectrum. Three optimum-exposure spectra were secured for each substance tested. The accuracy of frequency measurement was $\pm$ 1 cm^{-1} for the clear lines. The line intensities were determined visually on the basis of a 10-point scale. All the hydrocarbons we investigated were redistilled in vacuo without boiling in a sealed glass apparatus before photographing the spectra in order to free them of fluorescing impurities and suspended micro-particles.

Spectrum of d-α-pinene. This hydrocarbon was isolated from pine turpentine by carefully fractionating the latter in vacuo into a column with an efficiency of 50 theoretical trays and a reflux ratio of 40. The purest fractions of the α-pinene we secured were redistilled under the same conditions. We used the fraction that possessed the following constants:

d_4^{20} 0.8578; n_D^{20} 1.4653; $[\alpha]_C$ 22.30°; $[\alpha]_D$ 28.46°; $[\alpha]_{Hg_j}$ 29.76°; $[\alpha]_{Hg_i}$ 56.71°; $\frac{a_v}{a_c}$ 1.132; $\frac{aF}{a_c}$ 1.969 for our research.

To judge from the physical properties, this fraction is the purest α-pinene; it yielded a very clear spectrum containing 45 lines:

207(3); 261(6,b); 305(5); 337(1)*; 388(5); 426(5); 464(5); 483(5); 566(7); 618(6); 667(10); 735(0)*; 771(7); 790(0); 819(3); 843(8); 888(3)*; 908(6); 929(3); 943(3); 954(6); 994(1)*; 1014(1); 1043(6); 1065(1); 1086(7); 1126(7); 1165(7); 1182(6)*; 1205(4); 1221(5); 1265(7); 1306(5); 1331(7); 1376(6); 1436(8); 1449(6); 1471(3); 1658(9s); 2836(7); 2875(8); 2920(9); 2958(7); 2990(8); 3027(6).

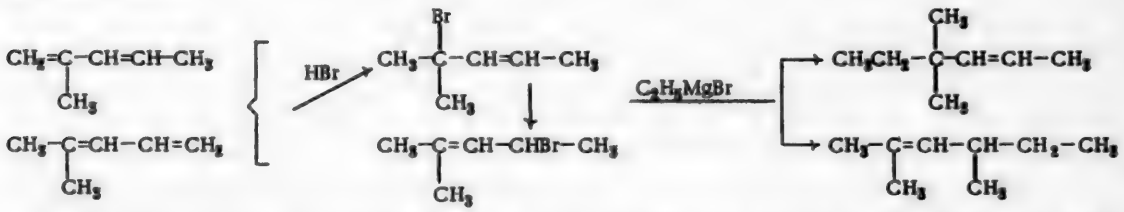
As against the previously known data, we have discovered 6 new lines. The rather good agreement of our data with the findings of G. Pigulevsky [1] is worthy of note. The line frequencies for α-pinene found by us differ from the findings of Dupont [3] and of Nevgi [4], being 4-5 cm^{-1} below the Dupont figures and about 3-4 cm^{-1} above the Nevgi figures.

* The asterisks denote new lines in this spectrum as well as in the subsequent ones.

XX. SYNTHESIS OF ALKENES AND ALKANES CONTAINING A QUATERNARY CARBON ATOM

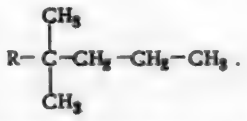
R. Ya. Levina, T. I. Tantsyreva, and A. A. Fainzilberg

The reaction of ethylmagnesium bromide with the hydrobromide of 2- or 4-methylpentadiene-1,3, which reacts in two isomeric forms, results, as we have shown previously [1], in the formation of a mixture of two isomeric alkenes (70% of the theoretical yield): 4,4-dimethylhexene-2 and 2,4-dimethylhexene-2, the former constituting 40% of the alkene mixture:

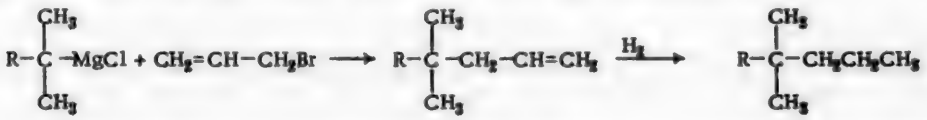


The isomeric alkanes, 2,4-dimethylhexane and 3,3-dimethylhexane, produced in the hydrogenation of the resulting alkene mixture, were separated by fractionation into a column.

The same series of reactions in which other organomagnesium compounds (n-propylmagnesium bromide, isopropylmagnesium bromide, and n-butylmagnesium bromide) were used resulted in the formation of a mixture of alkanes, which included homologs of 3,3-dimethylhexane—alkanes containing a quaternary carbon atom—the general structure of which is:



For the purposes of identification (by the Raman spectrum method), each of these alkanes had to be synthesized by another method. Hydrocarbons of this structure can be synthesized by employing a reaction of allyl bromide with the respective tert-alkylmagnesium chloride, followed by hydrogenation of the products of this reaction— α-ethylenic hydrocarbons that contain a quaternary carbon atom (4,4-dimethylalkenes-1).



The reaction of tert-alkylmagnesium chlorides with an allyl halide has been described in several papers as a method of synthesizing 4,4-dimethylalkenes-1. Whitmore [2], for example, secured a high yield of 4,4-dimethylpentene-1 (R = CH_3) by reacting tert-butylmagnesium chloride with allyl bromide at 5°, and by adding the two reagents in the inverse order. When the reaction is carried out under ordinary conditions, the hydrocarbon yield drops to 5% of the theoretical [3]. Liberman and Kazansky [4], employing allyl chloride instead of the bromide and carrying out the reaction at 12-16°, secured 35% of the theoretical yield of 4,4-dimethylhexene-1 (R = C_2H_5).

In the present paper 4,4-dimethylheptene-1 (R = n-C_3H_7, 49% of the theoretical yield), 4,4,5-trimethylhexene-1 (R = iso-C_3H_7, 28% of the theoretical yield), and 4,4-dimethyloctene-1 (R = n-C_4H_9, 42% of the theoretical yield) have been synthesized by reacting the tert-alkylmagnesium chlorides with allyl bromide, the corresponding alkanes— 4,4-dimethylheptane, 2,3,3-trimethylhexane, and 4,4-dimethyloctane—being produced by hydrogenating the foregoing alkenes. The synthesized hydrocarbons distilled within a narrow temperature range—0.1 to 0.2° (into a column with an efficiency of 35 theoretical trays), with the exception of 4,4-dimethylheptene-1, which distilled in a 0.4° range.

Of the six synthesized hydrocarbons, two hydrocarbons (4,4-dimethyloctene-1 and 4,4-dimethyloctane, $C_{10}H_{20}$ and $C_{10}H_{22}$) are not described in the literature. Nor has the synthesis of the other four hydrocarbons (C_9H_{18} and C_9H_{20}) been described in the literature; the constants of three of them are given, however, in the handbooks of Egloff and Doss, with references to unpublished dissertations by Reid [5,6] and Kline [6], while Fenske [7] cited some constants (b.p. and n_D^{20}) of the fourth hydrocarbon (without describing or even mentioning the method of synthesis) in a paper on Raman spectra.

EXPERIMENTAL

The initial tertiary alcohols were prepared by reacting absolute acetone [8] with organomagnesium compounds (n-propylmagnesium bromide, isopropylmagnesium bromide, and n-butylmagnesium bromide). Acetone was added while the reaction mixture was chilled with ice; then the reaction mixture was heated and stirred for 3 hours and allowed to stand overnight; it was decomposed by pouring over ice and adding dilute (15%) acetic acid; the aqueous layer was extracted 5 times with ether. The alcohols produced: dimethylpropylcarbinol (I), dimethylisopropylcarbinol (II), and dimethylbutylcarbinol (III), their yields being 54, 41, and 71% of the theoretical, respectively, had the following constants:

I. B.p. 120.3° (770 mm); n_D^{20} 1.4087; d_4^{20} 0.8041; MR_D 31.40; calculated 31.43.

II. B.p. 117-118° (750 mm); n_D^{20} 1.4235; d_4^{20} 0.8294; MR_D 31.41; calculated 31.43.

III. B.p. 138-139° (742 mm); n_D^{20} 1.4185; d_4^{20} 0.8136; MR_D 36.04; calculated 36.05.

Literature data: (I) b.p. 122-123° (760 mm) [9]; (II) b.p. 120-121° (762 mm); n_D^{18} 1.4140; d_4^{20} 0.8208 [10]; (III) b.p. 139.4-140.4° (735 mm); n_D^{20} 1.4175; d_4^{20} 0.8119 [11].

The synthesized carbinols were converted into the corresponding tertiary chlorides (the yields being 80% of the theoretical): 2-chloro-2-methylpentane (IV), 2-chloro-2,3-dimethylbutane (V), and 2-chloro-2-methylhexane (VI) by the action of concentrated hydrochloric acid upon the icewater-chilled reagent (the reaction mixture was kept in the same chilling agent for 1.5 hours after the hydrochloric acid had been added). The constants of the synthesized chlorides were as follows:

IV. B.p. 105-107° (746 mm); n_D^{20} 1.4128; d_4^{20} 0.8610; MR_D 34.90; calculated 34.78.

V. B.p. 108-109° (760 mm); n_D^{20} 1.4212; d_4^{20} 0.8758; MR_D 34.93; calculated 34.78.

VI. B.p. 127-128° (753 mm); n_D^{20} 1.4193; d_4^{20} 0.8569; MR_D 39.69; calculated 39.39.

Literature data: (IV) b.p. 110-113° (760 mm); $n_D^{16.5}$ 1.4148; d_4^{15} 0.8678 [12]; (V) b.p. 112° (749 mm); d_4^{19} 0.8784 [13]; (VI) b.p. 130-135° (760 mm) [14].

Synthesis of 4,4-dimethylalkenes-1 (C_9H_{18} and $C_{10}H_{20}$). 2 ml of ethyl bromide was added to 12 g of magnesium, activated by heating with iodine and covered with 150 ml of absolute ether, to start the reaction, after which a 1:1 ether solution of the tertiary chloride (0.5 mole) was gradually added at a rate that did not exceed one drop per second. The reaction flask had to be gently heated to keep the ether boiling gently but evenly; after the chloride had been added, heating was continued until all the magnesium had disappeared. The ether solution of the organomagnesium compound (whose yield was determined by titration to be 70% of the theoretical) was transferred to a funnel by siphoning in a nitrogen atmosphere, after which it was added, a drop at a time, with stirring and chilling (external chilling to −11°) to a 1:1 ether solution of allyl bromide (0.5 mole). Stirring was continued for 2 hours at room temperature and 3 hours of heating. The product was decomposed by gradually pouring the reaction mixture over ice to which ammonium chloride had been added. After the ether extract had been processed in the usual manner and the ether had been driven off, the residue was heated with sodium and distilled over the sodium twice. The alkenes thus purified, which contained not a trace of halogen, were distilled over sodium into a column with an efficiency of 35 theoretical trays. The constants and yields* of the synthesized alkenes are given in Table 1. The figures in the literature are cited in Table 4.

4,4-Dimethylheptene-1: 5.745 mg substance: 18.010 mg CO_2; 7.405 mg H_2O. 6.070 mg substance: 19,035 mg CO_2; 7.800 mg H_2O. Found %: C 85.55, 85.60; H 14.43, 14.48. C_9H_{18}. Calc. %: C 85.71; H 14.29.

4,4-Dimethyloctene-1: 7.520 mg substance: 23.585 mg CO_2; 9.720 mg H_2O. 5.480 mg substance: 17.180 mg CO_2; 7.050 mg H_2O. Found %: C 85.59, 85.55; H 14.46, 14.40. $C_{10}H_{20}$. Calc.%: C 85.62; H 14.38.

Bromination of the synthesized 1-alkenes was effected in a chilled chloroform solution. After the reaction mixture had been processed in the usual manner and the chloroform had been driven off, the dibromides

* Based on the tertiary chloride.

TABLE 1

Constants of Alkenes with the General Structure of $RC(CH_3)_2CH_2CH=CH_2$

No.	R	Alkene	Boiling point	n_D^{20}	d_4^{20}	MR_D		Yield	
						Found	Calculated	(g)	% of theoretical
1	C_3H_7	4,4-Dimethylheptene-1	129.1-129.5° (764 mm)	1.4185	0.7324	43.45	43.30	31	49
2	iso-C_3H_7	4,4,5-Trimethylhexene-1	132.2-132.4° (760 mm)	1.4251	0.7494	43.10	43.30	17.5	28
3	C_4H_9	4,4-Dimethyloctene-1	152.5-152.6° (749 mm)	1.4231	0.7451	47.94	47.91	30	42

TABLE 2

Constants of Dibromides with the General Structure of $RC(CH_3)_2CH_2CHBrCH_2Br$

No.	R	Dibromide	Boiling point	n_D^{20}	d_4^{20}	MR_D	
						Found	Calculated
1	C_3H_7	1,2-Dibromo-4,4-dimethylheptane	87.5-88° (3 mm)	1.4972	1.4070	59.54	59.29
2	iso-C_3H_7	5,6-Dibromo-2,3,3-trimethylhexane	90.5-91 (3 mm)	1.5046	1.4320	59.24	59.29
3	C_4H_9	1,2-Dibromo-4,4-dimethyloctane	101 (3 mm)	1.4942	1.3590	64.31	63.91

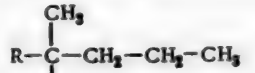
TABLE 3

Constants of Alkanes with the General Structure of $RC(CH_3)_2CH_2CH_2CH_3$

No.	R	Alkane	Boiling point at 760 mm	n_D^{20}	d_4^{20}	MR_D	
						Found	Calculated
1	C_3H_7	4,4-Dimethylheptane	134.3-134.4°	1.4076	0.7221	43.74	43.76
2	iso-C_3H_7	2,3,3-Trimethylhexane	136.2-136.4	1.4138	0.7323	43.73	43.76
3	C_4H_9	4,4-Dimethyloctane	157.4-157.6	1.4144	0.7347	48.44	48.38

were distilled in vacuo; the constants of the resultant dibromides are given in Table 2.

The dibromides of 4,4-dimethylheptene-1, 4,4,5-trimethylhexene-1 and 4,4-dimethyloctene-1 are not described in the literature.

Synthesis of Alkanes (C_9H_{20} and $C_{10}H_{22}$) with the Structure of 

The alkenes were hydrogenated over platinized charcoal (15% platinum) at 160°. The constants of the synthesized alkanes after distillation over sodium into a column with an efficiency of 35 theoretical trays is given in Table 3. The figures in the literature are cited in Table 4.

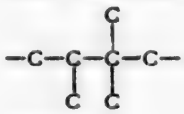
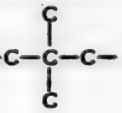
We see from the figures in Tables 1 and 3 that in each pair of isomers, C_9H_{18} (Nos. 1 and 2) and C_9H_{20} (Nos. 1 and 2), (where R = n-C_3H_7 and iso-C_3H_7), the hydrocarbons with a more highly branched structure, containing the  group, possess higher constants than the isomeric hydrocarbons with the  structure.

TABLE 4

Data in the Literature

No.	Hydrocarbon	B.p.	n_D^{20}	d_4^{20}	Remarks
1	4,4-Dimethylheptene-1	130.0-130.7° (740 mm)	1.4175	0.7489	Quoted from Egloff's handbook [5]; not described in the periodical literature.
2	4,4,5-Trimethylhexene-1	133.7-134.7 (760 mm)	1.4230	0.7528	Ditto
3	4,4-Dimethyloctene-1	—	—	—	Not described in the literature
4	4,4-Dimethylheptane	135.2 (760 mm)	1.4076	—	[7]
5	2,3,3-Trimethylhexane	137.4-137.6 (760 mm)	1.4141	0.7374	Quoted from Doss's handbook [6]; not described in the periodical literature.
6	4,4-Dimethyloctane	—	—	—	Not described in the literature

Hence, the isomeric hydrocarbons we have synthesized exhibit the characteristic pattern of behavior in the changes of their physical properties that is present, to judge by the data in the literature, in the isomeric hydrocarbons C_8H_{16} [15] (3,3-dimethylhexene-1 and 3,3,4-trimethylpentene-1) and C_8H_{18} [16] (3,3-dimethylhexane and 2,3,3-trimethylpentane), which have similarly branched carbon skeletons.

SUMMARY

1. Three ethylenic hydrocarbons with a quaternary carbon atom—4,4-dimethylpentene-1, 4,4,5-trimethylhexene-1, and 4,4-dimethyloctene-1 — have been synthesized by reacting tertiary alkylmagnesium chloride with allyl bromide, the yields being 49, 28, and 42% of the theoretical, respectively, based on the original tertiary chloride.

2. The synthesized alkenes have been identified as their dibromides (not described in the literature).

3. Alkanes with a quaternary carbon atom (C_9H_{20} and $C_{10}H_{22}$) — 4,4-dimethylheptane, 2,3,3-trimethylhexane, and 4,4-dimethyloctane—have been produced by hydrogenating the synthesized alkenes catalytically.

4. All the synthesized hydrocarbons have been collected within a narrow temperature range (0.1-0.2°, the range being 0.4° in only one instance) after distillation into a column with an efficiency of 35 theoretical trays and have been determined by accurate constants.

5. 4,4-Dimethyloctene-1 and 4,4-dimethyloctane have not been described in the literature. Only incomplete constants (b.p. and n_D^{20}) are cited in the literature for 4,4-dimethylheptane, without a description, or even a mention of the method of synthesis employed. The other hydrocarbons have not been published in the periodical literature, their constants being found only in handbooks, with references to unpublished foreign dissertations.

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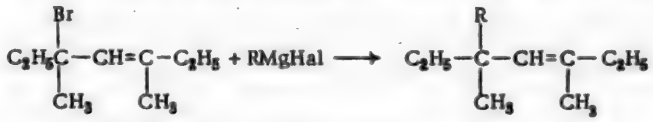
July 19, 1950

The N.D.Zelinsky Laboratory of Organic Chemistry of the M.V.Lomonosov State University of Moscow, Awarded the Order of Lenin.

XXI. HYDROBROMIDES OF DIENES IN THE SYNTHESIS OF OLEFINS AND PARAFFINS WITH A QUATERNARY CARBON ATOM

R. Ya. Levina and N. P. Shusherina

In our preceding report [1] we described the reaction of organomagnesium compounds (methylmagnesium iodide and ethylmagnesium bromide) with the unsaturated tertiary bromide 5-brom-3,5-dimethylheptene-3 (I), the structure of which excludes the possibility of any allyl rearrangement:

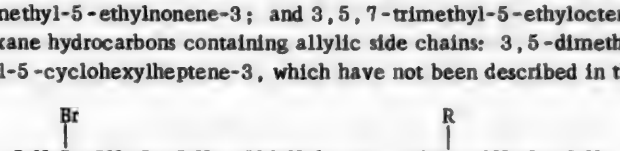


(I) (where R = CH_3 and C_2H_5)

The structure of the products of this reaction— the unsaturated hydrocarbons 3,5,5-trimethylheptene-3 and 3,5-dimethyl-5-ethylheptene-3 — was established by oxidizing them. Hydrogenating these synthesized alkenes yielded the respective alkanes— 3,3,5-trimethylheptane and 3,5-dimethyl-3-ethylheptane—their possession of a quaternary carbon atom being demonstrated by an analysis of their Raman spectra. Thus, the reaction of the tertiary allylic bromide 5-bromo-3,5-dimethylheptene-3 with organomagnesium compounds proved to be a convenient method of synthesizing hydrocarbons that are difficult of access and are not described in the literature: the 3,5-dimethyl-5-ethylalkenes-3 (the yield being 30% of the theoretical), and from them their corresponding alkanes.

In the present paper this reaction has been utilized to synthesize alkenes of higher molecular weight: two dodecenes and two tridecenes, hydrogenation of these alkenes yielding the corresponding dodecanes and tridecanes.

The reaction of 5-bromo-3,5-dimethylheptene-3 (I) with propyl-, isopropyl-, butyl-, and isobutylmagnesium bromides synthesized the following alkenes with a quaternary carbon atom that have not been described in the literature: 3,5-dimethyl-5-ethyloctene-3; 3,5,6-trimethyl-5-ethylheptene-3; 3,5-dimethyl-5-ethylnonene-3; and 3,5,7-trimethyl-5-ethyloctene-3. The corresponding aromatic and cyclohexane hydrocarbons containing allylic side chains: 3,5-dimethyl-5-phenylheptene-3 and 3,5-dimethyl-5-cyclohexylheptene-3, which have not been described in the literature



(I) (A)

(where R = C_3H_7, C_4H_9, iso-C_3H_7, iso-C_4H_9, C_6H_5, C_6H_{11})

have likewise been synthesized by reacting the same tertiary allylic bromide (I) with phenylmagnesium bromide and cyclohexylmagnesium chloride.

The presence of a quaternary carbon atom between the double bond and the radical R in the synthesized hydrocarbons of the general structure (A) was established by the behavior of one of them (R = C_6H_5), 3,5-dimethyl-5-phenylheptene-3 (II), a homolog of allylbenzene, in a contact isomerization reaction. As one of the present authors has demonstrated previously, allylbenzene and its homologs readily undergo a characteristic conversion into propenylbenzene and its homologs, whose physical and chemical properties differ considerably

from those of the initial hydrocarbons when placed in contact with alumina [2] and chromic oxide on alumina [3] at 250°. If there is a quaternary carbon atom deprived of a hydrogen located between the double bond and the aromatic radical, the double bond cannot be shifted, of course. As a matter of fact, when 3,5-dimethyl-5-phenylheptene-3 was passed over chromic oxide on alumina (at 250°), it did not suffer any isomerization, which is direct confirmation of the structure of this hydrocarbon and, hence of the cited hydrocarbons of structure (A), synthesized in the same reaction:

$$C_6H_5CH_2CH{=}CH_2 \xrightarrow{Cr_2O_3/Al_2O_3} C_6H_5CH{=}CH{-}CH_3$$

$$C_6H_5C(C_2H_5)(CH_3)-CH{=}C(CH_3)-C_2H_5 \xrightarrow{Cr_2O_3/Al_2O_3} \text{no change}$$

(II)

The structure of the synthesized alkenes was likewise confirmed by analyzing the oxidation products of two of them: 3,5-dimethyl-5-ethyloctene-3 and 3,5-dimethyl-5-ethynonene-3.

Large amounts of hydrogen bromide were liberated when the alkenes were brominated in an ether solution; the products of this reaction proved to be the respective unsaturated monobromides. As we know from the literature, the splitting out of hydrogen bromide from secondary-tertiary dibromides results in the formation of unsaturated monobromides of the vinyl type:

$$R-C(R)(Br)-CH(Br)-R' \xrightarrow{-HBr} R-C(R)=C(Br)-R'$$

(where R = CH_3, R' = CH_3 [6], C_2H_5 [7] or iso-C_3H_7 [8])

Thus, the unsaturated dibromides that are the products of the bromination of the isomeric alkenes synthesized in the present research are apparently homologs of vinyl bromide (III):

$$C_2H_5C(R)(CH_3)-CH{=}C(CH_3)-C_2H_5 \xrightarrow{Br_2} \left[C_2H_5C(R)(CH_3)-CH(Br)-C(Br)(CH_3)-C_2H_5\right] \xrightarrow{-HBr} C_2H_5-C(R)(CH_3)-C(Br){=}C(CH_3)-C_2H_5$$

(A) (III)

(where R = C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9)

The specific nature of the bromination reaction is borne out by the structure of the synthesized alkenes as trisubstituted ethylenes (containing the $-CH{=}C<$ group).

Hydrogenation of the synthesized alkenes, and of the cyclohexane hydrocarbon with an unsaturated side chain, resulted in the synthesis of the corresponding alkanes (A'): 3,5-dimethyl-5-ethyloctane; 2,3,5-trimethyl-3-ethylheptane; 3,5-dimethyl-5-ethylnonane; 2,4,6,-trimethyl-4-ethyloctane, and 3,5-dimethyl-3-cyclohexylheptane (none of which is described in the literature):

$$C_2H_5C(R)(CH_3)-CH{=}C(CH_3)-C_2H_5 \xrightarrow{H_2} C_2H_5C(R)(CH_3)-CH_2-CH(CH_3)-C_2H_5$$

(A) (A')

(where R = C_3H_7, C_4H_9, iso-C_3H_7, iso-C_4H_9, and C_6H_{11})

Examination of the Raman spectra of the synthesized alkanes confirmed their having a quaternary carbon atom.

EXPERIMENTAL

The initial tertiary allyl bromide, 5-bromo-3,5-dimethylheptene-3 (I), was produced by adding one molecule of hydrogen bromide at the 1,2 and 1,4 positions to a mixture of dienes: 3,5-dimethylheptadiene-2,4 and 4-methyl-2-ethylhexadiene-1,3. The synthesis and analysis of the initial dienes and the synthesis of the hydrobromide (I) from them have been described in preceding reports [1,4].

Synthesis of unsaturated hydrocarbons with a quaternary carbon atom (A). 5-Bromo-3,5-dimethylheptene-3 (I) was reacted with organomagnesium compounds (RMgHal, where R = C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, C_6H_5, and C_6H_{11}) under the conditions we have described previously [1] (for the reaction of this bromide with methylmagnesium iodide), i.e., with the proportions of 5-bromo-3,5-dimethylheptene-3 to the alkyl

halide and the magnesium being 1:1.5:1.5, employing constant stirring and chilling of the reaction mixture to −40 to −50°, followed by its heating for 6 hours. The products of the reaction of the initial unsaturated hydrobromide (I) with the propyl-, isopropyl-, butyl-, and isobutyl-magnesium bromides were processed in the usual manner and then fractionated * over sodium into a column with an efficiency of 25 theoretical trays. The products of the reactions of the hydrobromide (I) with the phenylmagnesium bromide and the cyclohexylmagnesium chloride were distilled (over sodium) in vacuo, after the low-boiling fractions * had been driven off at atmospheric pressure. The allylbenzene homolog (II), produced in the first of these reactions (R = C_6H_5), was freed of its traces of diphenyl by freezing it twice before the vacuum distillation. The constants and the yields of the synthesized unsaturated hydrocarbons (A) are given in Table 1, the analysis data being given in Table 4.

TABLE 1

Hydrocarbons of the General Structure $R-\underset{CH_3}{\overset{C_2H_5}{C}}-CH=\underset{CH_3}{\overset{}{C}}-C_2H_5$

Where R is	Name of hydrocarbon	B.p.	n_D^{20}	d_4^{20}	MR_D		Yield, % of theoretical
					Found	Calc.	
C_3H_7	3,5-Dimethyl-5-ethyloctene-3	191.4° (756 mm)	1.4432	0.7800	56.96	57.17	40
iso-C_3H_7	3,5,6-Trimethyl-5-ethylheptene-3	194.5-195 (754 mm)	1.4492	0.7913	56.61	57.17	27
C_4H_9	3,5-Dimethyl-5-ethylnonene-3	211.5-212 (766 mm)	1.4457	0.7850	61.85	61.76	41
iso-C_4H_9	3,5,7-Trimethyl-5-ethyloctene-3	206.5-207.5 (765 mm)	1.4446	0.7833	61.77	61.76	30
C_6H_5	3,5-Dimethyl-5-phenylheptene-3	104-104.5 (4 mm) 255-256 (755 mm)	1.5313	0.9244	67.75	67.40	18
C_6H_{11}	3,5-Dimethyl-5-cyclohexylheptene-3	97-97.5 (1.5 mm)	1.4790	0.8660	68.23	68.00	41

Oxidation of the alkenes (A) with potassium permanganate was effected in an acetone solution in the cold, the acetone having been previously heated with potassium permanganate itself. Oxidizing the alkene 3,5-dimethyl-5-ethyloctene-3, synthesized by reacting the unsaturated hydrobromide (I) with propylmagnesium bromide, yielded (after the customary processing) an acid with a b.p. of 213-215°, the composition of which was $C_8H_{16}O_2$, to judge from the analysis of its silver salt, thus corresponding to methylethylpropylacetic acid (b.p. 215-220° [9].)

0.1161 g substance: 0.0502 g Ag. Found %: Ag 43.30. $C_8H_{15}O_2Ag$. Calculated %: Ag 43.01.

Oxidizing the 3,5-dimethyl-5-ethylnonene-3 synthesized by reacting the unsaturated hydrobromide with butylmagnesium bromide yielded an acid, whose silver salt proved upon analysis to be a salt of methylethylbutylacetic acid.

1.1078 g substance: 0.0450 g Ag. Found %: Ag 41.07. $C_9H_{17}O_2Ag$. Calculated %: Ag 40.70.

The oxidation results confirmed the structure of the two hydrocarbons as 3,5-dimethyl-5-ethyloctene-3 and 3,5-dimethyl-5-ethylnonene-3, respectively.

Bromination of the alkenes (A) was effected in a chilled ether solution and was accompanied by the evolution of considerable hydrogen bromide. After the bromination products had received the usual treatment, they were vacuum-distilled in a current of nitrogen. The constants of the synthesized unsaturated monobromides (III), apparently of the vinyl type, are listed in Table 2. The monobromides darkened considerably upon standing.

* In every case, the initial mixture of dienes was recovered as a low-boiling distillation fraction (b.p. 135-145°), constituting 30-40% of the dienes (b.p. 136-142° [1]) used for the hydrobromination reaction. Thus, the reaction of the unsaturated tertiary bromide (I) with organomagnesium compounds involved the splitting out of hydrogen bromide from it.

TABLE 2

Unsaturated Monobromides of the General Structure R–C(C$_2$H$_5$)(CH$_3$)–CBr=C(CH$_2$)–C$_2$H$_5$

Where R is	B.p.	n_D^{20}	d_4^{20}	MR_D	
				Found*	Calc.
C_3H_7	93-95° (12 mm)	1.4808	1.0909	64.47	64.91
iso-C_3H_7	89-90 (4 mm)	1.4917	1.0970	65.46	64.91
C_4H_9	102-104 (2 mm)	1.4860	1.0748	69.75	69.56
iso-C_4H_9	94-95 (3 mm)	1.4830	1.0590	70.46	69.56

* The substantial discrepancies (0.4-0.9) between the experimental molecular refractions of the monobromides and the calculated values may be due to traces of the respective dibromides; whenever we distilled the bromination products of the alkenes, we secured high-boiling fractions that contained a mixture of unsaturated monobromides and dibromides.

Analysis of the bromination product of 3,5-dimethyl-5-ethyloctene-3 confirmed that its structure was that of the unsaturated monobromide 4-bromo-3,5-dimethyl-5-ethyloctene-3.

8.80 mg substance: 7.56 mg H_2O; 18.80 mg CO_2; 2.86 mg Br_2. 10.31 mg substance; 8.61 mg H_2O; 22.04 mg CO_2; 3.38 mg Br_2. Found %: C 58.30, 58.34; H 9.61, 9.35; Br 32.6, 32.8. $C_{12}H_{23}Br$. Calculated %: C 58.18; H 9.38; Br 32.35.

Behavior of the synthesized allylbenzene homolog (II) in contact with chromic oxide on alumina. The allylbenzene homolog 3,5-dimethyl-5-phenylheptene-3 (II), synthesized by reacting the unsaturated hydrobromide (I) with phenylmagnesium bromide, was passed over an isomerizing (shifting the double bond) contact agent, consisting of chromic oxide on alumina [3] at 250° in a current of nitrogen. After the resulting catalyzate had been distilled over sodium, its constants were the same as those of the initial hydrocarbon (Table 1): b.p. 255-256° at 752 mm; n_D^{20} 1.5320; d_4^{20} 0.9249. Hence, 3,5-dimethyl-5-phenylheptene-3 underwent no change under the specified conditions, i.e.,

TABLE 3

Hydrocarbons of the General Structure R–C(C$_2$H$_5$)(CH$_3$)–CH$_2$–CH(CH$_3$)–C$_2$H$_5$

Where R is	Hydrocarbon	Boiling point	n_D^{20}	d_4^{20}	MR_D	
					Found	Calculated
C_3H_7	3,5-Dimethyl-5-ethyloctane.....	188.5-189° (750 mm)	1.4315	0.7695	57.23	57.60
iso-C_3H_7.....	2,3,5-Trimethyl-3-ethylheptane.....	197.5-198° (759 mm)	1.4387	0.7820	57.25	57.61
C_4H_9.....	3,5-Dimethyl-5-ethylnonane.....	213-214° (760 mm)	1.4356	0.7761	62.06	62.23
iso-C_4H_9.....	2,4,6-Trimethyl-4-ethyloctane.....	79-80° (7 mm)	1.4349	0.7760	61.98	62.23
C_6H_{11}.....	3,5-Dimethyl-5-cyclohexylheptane..	98-99° (2 mm)	1.4679	0.8515	68.73	69.27

it did not undergo the conversion into propenylbenzene (and its homologs) that is characteristic of allylbenzene (and its homologs), which proves that the structure of this hydrocarbon contains a quaternary carbon atom located between the double bond and the aromatic nucleus.

Catalytic hydrogenation of the alkenes (A) and of the homolog of allylcyclohexane (R = C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, and C_6H_{11}) was effected at 170° over platinized charcoal (15% Pt). The catalyzates did not decolorize bromine water or an aqueous solution of potassium permanganate. The resultant alkanes, containing a quaternary carbon atom, were distilled over sodium into a column with an efficiency of 25 theoretical trays, while the cyclohexane hydrocarbon (with a quaternary carbon atom in the side chain) was distilled in vacuo. The constants of all these hydrocarbons (A') are listed in Table 3, their analysis data being found in Table 4.

When we investigated the Raman spectra* of the synthesized alkanes, we found more or less intense frequencies in the ~1200 cm^{-1} region, an indication (according to B. I. Stepanov [5]) that the hydrocarbon molecule contains a quaternary carbon atom, which agrees satisfactorily with the values of the fully symmetrical frequencies present in the spectra in the ~700 cm^{-1} region [10]. Thus, the spectrum of 3,5-dimethyl-5-ethyloctane (R = = C_3H_7) [10] exhibited the frequencies 1200(2), 1213(1.5), and 1249(1), as well as the fully symmetrical frequency 728(6; b); the spectrum of 2,3,5-trimethyl-3-ethylheptane (R = iso-C_3H_7) exhibiting the frequency 1219(2.5) and

* We are indebted to V. M. Tatevsky and E. G. Treshchova for having carried out the optical investigations.

TABLE 4

	Hydrocarbon	mg substance	mg CO_2	mg H_2O	Found % C	Found % H	Calculated % C	Calculated % H	General Formula
Alkenes	3,5-Dimethyl-5-ethyloctene-3	5.540	17.112	6.952	85.63	14.23	85.63	14.37	$C_{12}H_{24}$
		6.590	20.682	8.497	85.59	14.43			
	3,5,6-Trimethyl-5-ethylheptene-3	7.020	22.020	8.995	85.55	14.34	85.63	14.37	$C_{12}H_{24}$
		6.710	21.050	8.560	85.57	14.28			
	3,5-Dimethyl-5-ethylnonene-3	5.915	18.570	7.605	85.62	14.39	85.62	14.38	$C_{13}H_{26}$
		4.385	13.760	5.625	85.58	14.36			
	3,5,7-Trimethyl-5-ethyloctene-3	2.860	8.980	3.670	85.63	14.36	85.62	14.38	$C_{13}H_{26}$
		5.020	15.760	6.450	85.62	14.38			
Alkanes	3,5-Dimethyl-5-ethyloctane	7.105	22.077	9.742	84.76	15.34	84.62	15.38	$C_{12}H_{26}$
		3.955	12.274	5.397	84.64	15.27			
	2,3,5-Trimethyl-3-ethylheptane	4.800	14.872	6.609	84.50	15.30	84.62	15.38	$C_{12}H_{26}$
		4.670	14.477	6.422	84.55	15.28			
	3,5-Dimethyl-5-ethylnonane	5.860	18.15	9.818	84.52	15.46	84.69	15.31	$C_{13}H_{28}$
		8.220	25.42	13.70	84.60	15.40			
	2,4,6-Trimethyl-4-ethyloctane	4.375	13.577	6.004	84.64	15.25	84.69	15.31	$C_{13}H_{28}$
		4.464	13.871	6.098	84.75	15.18			

the fully symmetrical frequency 692(10); and the spectrum of 3,5-dimethyl-5-ethylnonane (R = C_4H_9) exhibiting the frequency 1200(2;b) and the fully symmetrical frequency 732(3;b).

SUMMARY

1. A series of alkenes containing a quaternary carbon atom: 3,5-dimethyl-5-ethyloctene-3; 3,5,6-trimethyl-5-ethylheptene-3; 3,5-dimethyl-5-ethylnonene-3; and 3,5,7-trimethyl-5-ethyloctene-3, as well as aromatic and cyclohexane hydrocarbons with a quaternary carbon atom in a side chain: 3,5-dimethyl-5-phenylheptene-3 and 3,5-dimethyl-5-cyclohexylheptene-3, has been synthesized by reacting an unsaturated tertiary bromide of the allylic type, 5-bromo-3,5-dimethylheptene-3, with organomagnesium compounds (RMgHal, where R = C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, C_6H_5, and C_6H_{11}).

2. The presence of a quaternary carbon atom in the synthesized unsaturated hydrocarbons, located between the double bond and the radical R, has been established by analyzing the oxidation products of two hydrocarbons: 3,5-dimethyl-5-ethyloctene-3 and 3,5-dimethyl-5-ethylnonene-3 (R = C_3H_7 and C_4H_9) and by the passivity of 3,5-dimethyl-5-phenylheptene-3 (R = C_6H_5), a homolog of allylbenzene, when in contact with chromic oxide on alumina.

3. The structure of the synthesized unsaturated hydrocarbons as trisubstituted ethylenes (i.e., the presence of the $-CH=C<$ group in them) has been established by the production, during bromination, of unsaturated monobromides of the vinyl type, formed by the splitting out of hydrogen bromide from the normal bromination products – secondary-tertiary dibromides.

4. Several alkanes with a quaternary carbon atom: 3,5-dimethyl-5-ethyloctane; 2,3,5-trimethyl-3-ethylheptane; 3,5-dimethyl-5-ethylnonane; and 2,4,6-trimethyl-4-ethyloctane, as well as a cyclohexane hydrocarbon with a quaternary carbon atom in the side chain: 3,5-dimethyl-3-cyclohexylheptane, were produced by catalytically hydrogenating the synthesized unsaturated hydrocarbons.

5. The presence of a quaternary carbon atom in the synthesized alkanes has been confirmed by analysis of their Raman spectra.

6. The 11 hydrocarbons synthesized in the present research have not been described in the literature.

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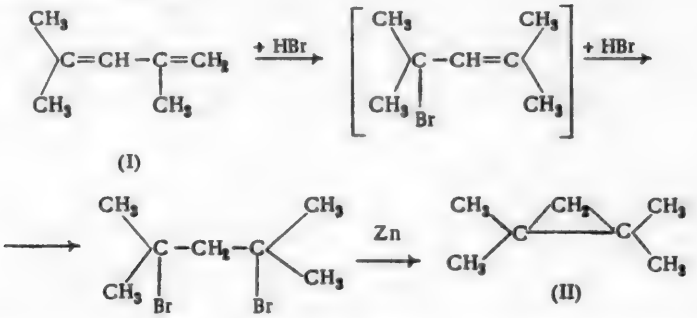
XXII. THE CONVERSION OF DIENES INTO CYCLOPROPANES

R. Ya. Levina and B. M. Gladshtein

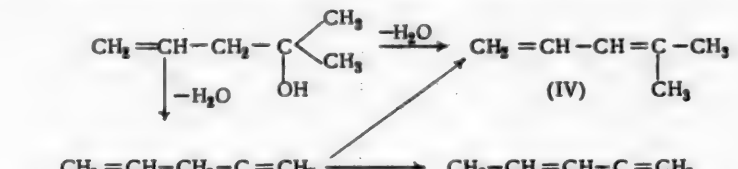
In one of our previous reports [1] we described a new method of producing a cyclopropane with two quaternary carbon atoms—producing 1,1,2,2-tetramethylcyclopropane (II) from an asymmetrical diene of the conjugated type: 2,4-dimethylpentadiene-1,3 (I):



In the present research we have shown that other dienes containing conjugated double bonds, whose structure is a branched one, can also be converted into the respective cyclopropanes by adding two molecules of hydrogen bromide (giving rise to 1,3-dibromides) and splitting two atoms of bromine from the latter by means of zinc dust (Gustavson reaction [2]).

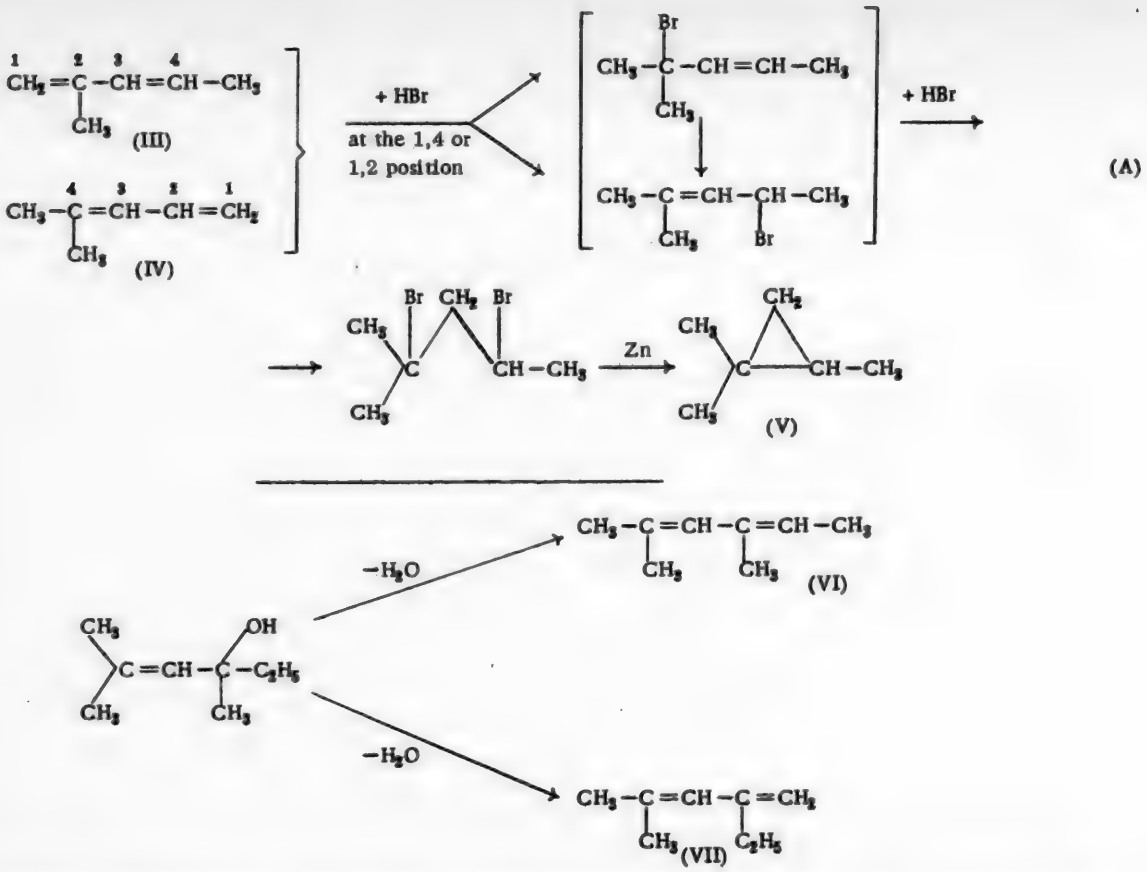
The initial branched dienes were produced by dehydrating unsaturated tertiary alcohols—dimethylallylcarbinol, 2,4-dimethylhexen-2-ol-4, and 3,5-dimethylhepten-3-ol.

Dehydration of dimethylallylcarbinol was effected by passing it over chromic oxide on alumina, employing the method developed previously by one of the present authors [3], which furnishes a high yield of a mixture of isomeric conjugated C_6H_{10} dienes — 2-methylpentadiene-1,3 (III) and 4-methylpentadiene-1,3 (IV):

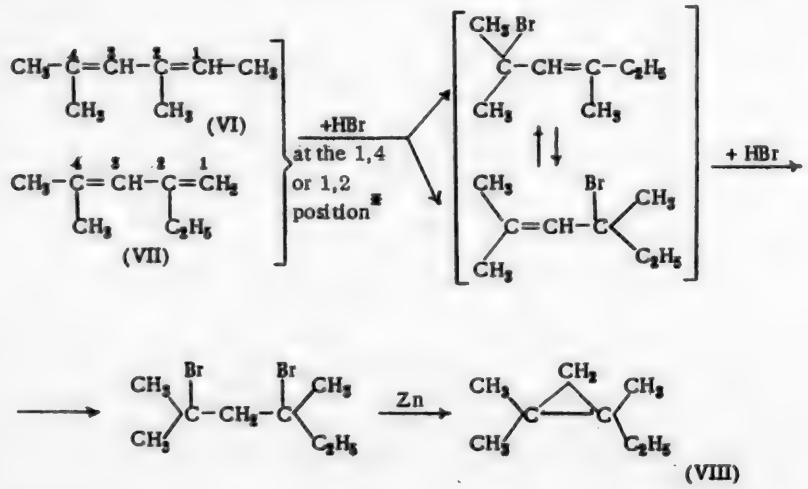


Adding the first molecule of hydrogen bromide to the mixture of these conjugated dienes at the 1,4 and 1,2 positions results in the formation of an allylic bromide, which can then react further in two isomeric forms, related by allyl rearrangement [4]; adding the second molecule of hydrogen bromide yields a 1,3-dibromide, the reaction of which with zinc dust yields 1,1,2-trimethylcyclopropane (V): (see (A) following page).

Dehydration of 2,4-dimethylhexen-2-ol-4 (produced by reacting mesityl oxide with ethylmagnesium bromide) was effected by simply distilling it, resulting in the production of a mixture of isomeric conjugated C_8H_{14} dienes with the same carbon skeleton—2,4-dimethylhexadiene-2,4 (VI) and 2-ethyl-4-methylpentadiene-1,3 (VII) [5]:

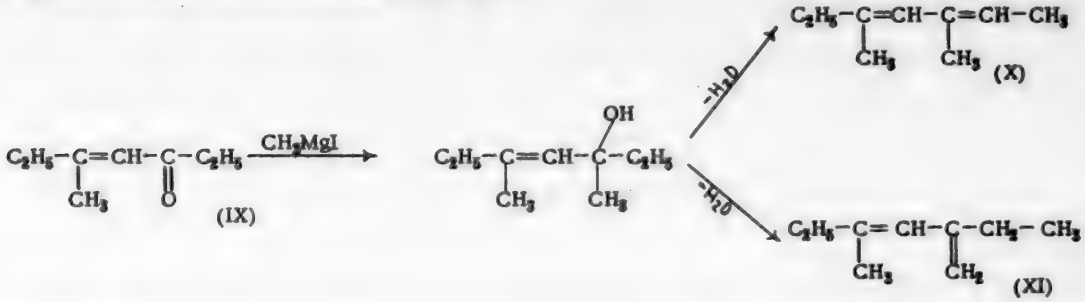


The addition of two molecules of hydrogen bromide to the resulting mixture of dienes yielded a 1,3-dibromide, the reaction of which with zinc dust yielding 1,1,2-trimethyl-2-ethylcyclopropane (VIII):

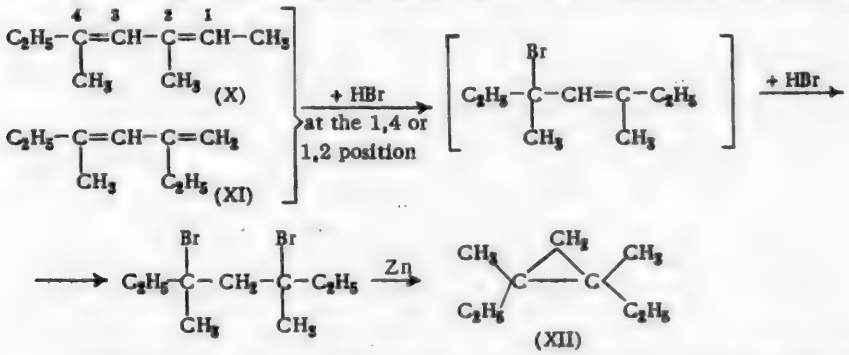


* The addition of the first molecule of hydrogen bromide at the 3,4 position to these conjugated branched dienes would have resulted in the formation of monobromides that were not of the allylic type, such monobromides not having been detected in any of the cases described in the literature.

Dehydration of 3,5-dimethylhepten-3-ol-5 (produced by reacting the "homomesitone" (IX) with methylmagnesium iodide [6]) was effected by heating and then distilling it, resulting in the formation of a mixture of isomeric conjugated C_9H_{16} dienes with the same carbon structure—3,5-dimethylheptadiene-2,4 (X) and 2-ethyl-4-methylhexadiene-1,3 (XI) [7]:

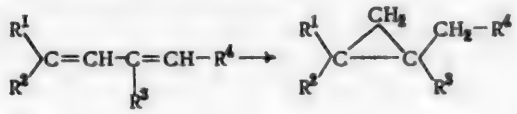


Adding a single molecule of hydrogen bromide to a mixture of these dienes at the 1,2 or 1,4 position results in the formation of an allylic unsaturated tertiary bromide, which exists in only one form (no allylic rearrangement taking place) [6]; the addition of more hydrogen bromide to this hydrobromide resulted in the formation of a 1,3-dibromide, whose reaction with zinc dust yielded a cyclopropane with two quaternary carbon atoms—1,2-dimethyl-1,2-diethylcyclopropane (XII), not described in the literature:



Study of the cyclization of ditertiary 1,3-dibromides, carried out for the first time in our previous and present papers, has convincingly shown that the Gustavson reaction (the action of zinc dust upon 1,3-dibromides) can be successfully employed with ditertiary dibromides, contrary to the opinion of Shortridge and Boord [9], these dibromides being transformed with good yields (50-80%) into cyclopropanes with two quaternary carbon atoms.

The results of the present research have likewise finally established the general nature of the new reaction we have proposed for the direct conversion of aliphatic branched conjugated dienes into homologs of cyclopropane with the same number of carbon atoms:



(where all the R's denote radicals or else one or two of them are hydrogen atoms).

EXPERIMENTAL

Production of a mixture of isomeric C_6H_{10} alkadienes—2-methylpentadiene-1,3 and 4-methylpentadiene-1,3. The procedure involved in the synthesis of dimethylallylcarbinol (67-70% of the theoretical yield), its catalytic dehydration over chromic oxide on alumina at 250°, and the analysis of the resultant dienes have been described in one of our preceding papers [3]. The synthesizing mixture of 2-methylpentadiene-1,3 (III) and 4-methylpentadiene-1,3 (IV) (59% of the theoretical yield) was distilled over sodium

into a column with an efficiency of 25 theoretical trays, after which its constants were as follows:

B.p. 72.5-75.5° (761 mm); n_D^{20} 1.4474; d_4^{20} 0.7147; MR_D 30.69; $C_6H_{10}F_2$; calculated 28.97; EM_D 1.72.

Figure given in the literature [10]: B.p. 73-75.8°.

Production of a mixture of isomeric C_8H_{14} alkadienes—2,4-dimethylhexadiene-2,4 and 2-ethyl-4-methylpentadiene-1,3. The reaction of mesityl oxide with ethylmagnesium bromide and the dehydration (by simple distillation) of the dimethylhexenol produced in this reaction were effected by the methods described in one of our preceding papers [11] (for the synthesis and dehydration of dimethylpentenol). The resultant mixture of dienes—2,4-dimethylhexadiene-2,4 (VI) and 2-ethyl-4-methylpentadiene-1,3 (VII), which differ only in the position of one of the double bonds (the yield being 60% of the theoretical, based on the mesityl oxide), possessed the following constants after distillation over sodium into a column with an efficiency of 25 theoretical trays:

B.p. 114-117.5° (760 mm); n_D^{20} 1.4461; d_4^{20} 0.7537; MR_D 39.00; $C_8H_{14}F_2$; Calc. 38.21; EM_D 0.79.

Figures given in the literature [12] for the individual components of this mixture of dienes, separated by distillation: 2,4-dimethylhexadiene-2,4 — b.p. 116° (752 mm) n_D^{22} 1.4540, d_4^{22} 0.7663; 2-ethyl-4-methylpentadiene-1,3 — b.p. 113-113.5° (752 mm) $n_D^{18.8}$ 1.4444, $d_4^{18.8}$ 0.7660.

Production of a mixture of isomeric C_9H_{16} alkadienes—3,5-dimethylheptadiene-2,4 and 2-ethyl-4-methylhexadiene-1,3. The synthesis of "homomesitone" (IX) (by the condensation of methyl ethyl ketone, using calcium carbide), the reaction of the product with methyl-magnesium iodide, the dehydration of the resultant dimethylheptenol by heating and distilling it, and the analysis of the dienes produced have been described in preceding reports [6,7]. The resultant mixture of dienes—3,5-dimethylheptadiene-2,4 (X) and 2-ethyl-4-methylhexadiene-1,3 (XI) (86% of the theoretical yield, based on the "homomesitone") had the following constants after distillation over sodium into a column with an efficiency of 25 theoretical trays:

B.p. 136-142° (760 mm); n_D^{20} 1.4474; d_4^{20} 0.7631; MR_D 43.52; $C_9H_{16}F_2$; calc. 42.83; EM_D 0.69.

Neither the 3,5-dimethylheptadiene-2,4 nor the 2-ethyl-4-methylhexadiene-1,3 has been described in the literature. In our previous researches [6,7] we secured two extreme fractions (b.p. 137.4-137.6° at 766 mm; n_D^{20} 1.4490, d_4^{20} 0.7645, EM_D 0.75 and b.p. 141-141.4° (740 mm), n_D^{20} 1.4522, d_4^{20} 0.7673, EM_D 0.86), representing the two stated constituents of this diene mixture, by careful fractionation over sodium of a hydrocarbon mixture produced in the same way into a column with an efficiency of 40 theoretical trays. Catalytic hydrogenation [7] of both the diene mixture (b.p. 136-142°) and the specified fractions thereof yielded the same alkane—3,5-dimethylheptane, proving that their carbon skeletons were identical.

Producing cyclopropanes from dienes. Hydrogen bromide, dried and freed of all traces of bromine, was passed through each diene mixture (C_6H_{10}, C_8H_{14}, and C_9H_{16}), chilled to -5° until saturation was complete. Two molecules of hydrogen bromide were added to 10 g of the dienes within 40-50 minutes (90-92% of the calculated quantity of hydrogen bromide being absorbed). The resultant dihydrobromides (1,3-dibromides, one secondary-tertiary and the other two ditertiary) were not isolated in the individual state, inasmuch as hydrogen bromide was split off when they were heated and distilled in vacuo, but reacted with zinc dust immediately after they had been produced. The dibromides were cyclized by constant stirring in ethyl alcohol (96%) with four times their weight of zinc dust. The cyclopropanes that were the products of these reactions were processed in the usual manner and then distilled over sodium into a column, the 1,1,2-trimethylcyclopropane (V) and the 1,1,2-trimethyl-2-ethylcyclopropane (VIII) synthesized from the C_6H_{10} and C_8H_{14} dienes, respectively, being distilled into a column with an efficiency of 40 theoretical trays, and the 1,2-dimethyl-1,2-diethylcyclopropane (XII) synthesized from the C_9H_{16} dienes being distilled into a column with an efficiency of 50 theoretical trays.

These cyclopropanes did not decolorize a solution of potassium permanganate and decolorized a solution of bromine in carbon tetrachloride very slowly. They exhibited the exaltation of the molecular refraction (0.72-0.98) characteristic of hydrocarbons containing a three-membered ring [1,8]. The constants and yields of the cyclopropanes are given in Table 1, their analyses being set forth in Table 2. Analysis of their Raman spectra indicated that the trimethylcyclopropane (V) and the dimethyldiethylcyclopropane (XII) contained no traces of ethylenic or diene hydrocarbons, while the trimethylethylcyclopropane (VIII) contained a small quantity (up to 5%) of a hydrocarbon having a double bond.

TABLE 1

Cyclopropanes	B.p.	n_D^{20}	d_4^{20}	MR_D		EM_D	Aniline point	Found	
				Found	Calc.			g.	% of theoretical, based on initial diene mixture
1,1,2-Trimethylcyclopropane	52.0-52.3° (760 mm)	1.3845	0.6861	28.68	27.70	0.98	47.2°	42	84
1,1,2-Trimethyl-2-ethylcyclopropane	103.6-104 (754 mm)	1.4160	0.7408	37.92	36.94	0.98	51.0	22	80
1,2-Dimethyl-1,2-diethylcyclopropane *	131.1-131.3 (768 mm)	1.4230	0.7595	42.28	41.56	0.72	58.0	48	81

* This hydrocarbon, not described in the literature, can exist in two stereoisomeric (cis and trans) forms whose boiling points are closer together. When 56 g of this hydrocarbon was distilled into a column with an efficiency of 50 theoretical trays, we secured 48 g of a fraction with b.p. of 131.1-131.3°, the remainder boiling up to 132.9°.

Data in the Literature:

1,1,2-Trimethylcyclopropane—b.p. 56-57° (750 mm); $n_D^{19.5}$ 1.3848; $d_4^{19.5}$ 0.6822; MR_D 28.81; EM_D 1.10 [13]; b.p. 52.1° (736 mm); n_D^{20} 1.3850; d_4^{20} 0.6853; MR_D 28.78; EM_D 1.08 [14].

1,1,2-Trimethyl-2-ethylcyclopropane—b.p. 103.5-104.5°; $n_D^{20.4}$ 1.4129; $d_4^{20.4}$ 0.7418; MR_D 37.69; EM_D 0.75 [15].

TABLE 2

Hydrocarbon	Wt, mg	CO_2, mg	H_2O, mg	Found (%)		Calculated %		General formula
				C	H	C	H	
1,1,2-Trimethylcyclopropane . .	4.120	12.920	5.290	85.53	14.37	85.63	14.37	C_6H_{12}
	4.840	15.210	6.207	85.71	14.35			
1,1,2-Trimethyl-2-ethylcyclopropane	3.290	10.320	4.240	85.62	14.42	85.62	14.38	C_8H_{16}
	4.630	14.520	5.960	85.58	14.41			
1,2-Dimethyl-1,2-diethylcyclopropane	7.100	22.310	9.130	85.71	14.39	85.63	14.37	C_9H_{18}
	6.120	19.230	7.880	85.70	14.30			

SUMMARY

1. The method we have developed for synthesizing cyclopropanes from conjugated dienes of iso structure (by adding two molecules of hydrogen bromide to the latter and then splitting bromine out of the resulting 1,3-dibromides by means of zinc dust) has been utilized to synthesize three homologs of cyclopropane containing one or two quaternary carbon atoms.

2. 1,1,2-Trimethylcyclopropane, 1,1,2-trimethyl-2-ethylcyclopropane, and 1,2-dimethyl-1,2-diethylcyclopropane (not described in the literature) have been synthesized in this manner, the respective yields being 61, 56, and 81% of the theoretical, based on the initial dienes.

3. The opinion of American chemists that ditertiary 1,3-dibromides cannot be cyclized in a Gustavson reaction has been disproved.

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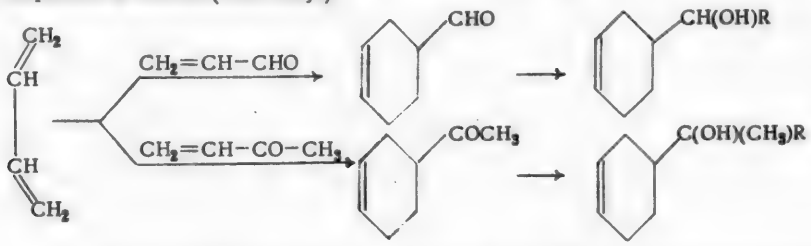
THE SYNTHESIS AND PROPERTIES OF SOME ISOMERS, HOMOLOGS, AND ANALOGS OF α-TERPINEOL BASED ON 1,3-DIENES

A.A.Petrov and N.P.Sopov

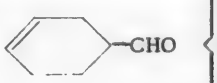
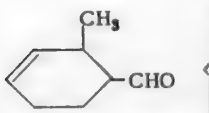
In earlier papers [1-3] the authors of this article investigated for the first time the condensation of 1,3-diene compounds with α,β-unsaturated ketones, which results in the synthesis of hydroaromatic ketones. These syntheses opened up a convenient transition from dienes to hydroaromatic alcohols of the α-terpineol type. This method had not been discussed in the literature prior to that time, though there were isolated references to the production of secondary hydroaromatic alcohols from dienes. Ethyl-(2,5-dimethylcyclohexen-3-yl)-carbinol was synthesized, for example, by reacting C_2H_5MgI with the condensation product of hexadiene-2,4 and crotonaldehyde [4], while several bicyclic alcohols were synthesized by reacting organomagnesium compounds with the condensation products of cyclohexadiene and cyclopentadiene with acrolein [5,6]. Inasmuch as only very few secondary hydroaromatic alcohols have been synthesized by this method, we included this synthesis in our research program.

The present paper describes the synthesis of secondary and tertiary hydroaromatic alcohols from 1,3-diene compounds as follows (for divinyl):

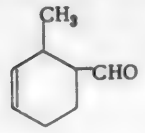


All the hydroaromatic aldehydes synthesized by us for this research have already been described in the literature. The condensation product of divinyl and acrolein, formylcyclohexene-3, has been described in detail by Chayanov [7]. 2-Methylformylcyclohexene-3 was first described by B.A.Arbuzov and his associates [4]. The constants of the aldehydes we used in our research are compared in Table 1 with the figures given in the literature.

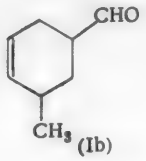
TABLE 1

Substance	B.p.	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calc.	Reference
	58-58.5° (20 mm)	0.9725	1.4732	31.78	31.87	
	52-53 (12 mm)	0.9650	1.4725	31.99	31.87	[7]
	70.5-71 (20 mm)	0.9528	1.4715	36.45	36.49	
	56-58 (11 mm)	0.9435	1.4653	36.35	36.49	[8]
	73.5-74.5 (20 mm)	0.9490	1.4732	36.72	36.49	
	64-66 (12 mm)	0.9630 (at 13°)	–	–	–	[6,10]
	104-104.5 (20 mm)	1.1589	1.5033	36.89	36.73	[3]

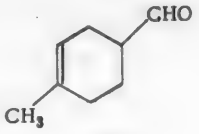
Condensation of acrolein with piperylene and isoprene might be expected to yield two products in each case:



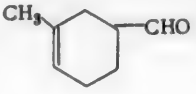
(Ia)



(Ib)



(IIa)



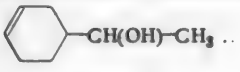
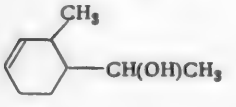
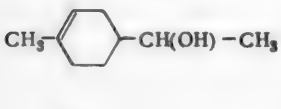
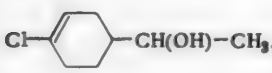
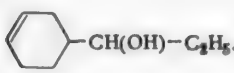
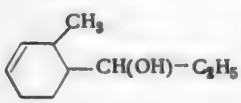
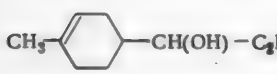
(IIb)

The structure of the aldehyde synthesized from acrolein and piperylene was first established by one of the present authors by oxidizing it to 2-methylcyclohexene-3-carboxylic acid with a chromic acid mixture [9]. The same acid was secured in crystalline form by oxidizing this aldehyde with moist silver oxide [8]. This proved that the substance had an "ortho" structure (Ia).

We established the structure of the condensation product of acrolein and isoprene by oxidizing it with moist silver oxide to crystalline 4-methylcyclohexene-3-carboxylic acid.

The structure of the aldehyde synthesized from chloroprene was not established, though there is every reason to believe that it has a "para" structure [3].

TABLE 2

Substance	Boiling point	d_4^{20}	n_D^{20}	MR_D		Reference
				Found	Calculated	
	93-93.5° (20 mm)	0.9592	1.4842	38.53	38.0	
	102-102.5° (20 mm)	0.9492	1.4834	42.21	42.62	
	106.25 (20 mm)	0.9421	1.4832	42.53	42.62	
	212-213° (760 mm)	0.942 (at 19°)	1.4836 (at 19°)	42.55	42.62	[11]
	124.5° (20 mm)	1.1194	1.5060	42.65	42.84	
	104-104.5 (20 mm)	0.9503	1.4832	42.16	42.62	
	111.5-112 (20 mm)	0.9406	1.4830	46.83	47.24	
	116.5-117° (20 mm)	0.9374	1.4828	46.98	47.24	

The only one of the secondary alcohols we synthesized that is described in the literature is methyl-(4-methylcyclohexen-3-yl)-carbinol. It was synthesized by reducing 4-methylacetylcyclohexene-(3) with sodium in alcohol [11].

The following conclusions may be drawn from a comparison of the constants of the substances listed in the table. Introducing a methyl group into the first compound listed in the table raises its boiling point, lowers its specific gravity, and has but little influence upon its refractive index. Compounds with "ortho" substituents have a lower boiling point and a higher specific gravity than "para" compounds. Substituting an ethyl group for the methyl group in the side chain (attached to the alcohol group) raises the boiling point (some 10°) and lowers the specific gravity, the change in the refractive index being insignificant. Substituting chlorine for the

methyl group raises the boiling point, the specific gravity, and the refractive index considerably. All the secondary alcohols we synthesized were fragrant. The alcohols that had no methyl group attached to the ring had an alcoholic odor. The alcohols in which the methyl group was in the "ortho" position had a sweetish odor. The alcohols with an ethyl group in the side chain had various shades of a mint odor. Methyl-(4-methylcyclohexen-3-yl)-carbinol had an odor that resembled that of α-terpineol (flower fragrance) most closely.

Of the chemical properties of the synthesized secondary alcohols, we investigated their behavior in the presence of bromine and in acetylation and oxidation. We were unable to secure crystalline substances by the action of bromine. Acetylation with acetic anhydride yielded three acetates, the constants of which are given in Table 3.

TABLE 3

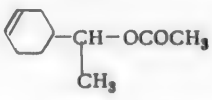
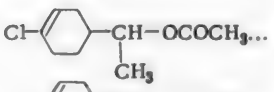
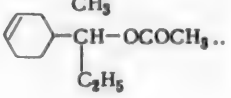
Formula	B.p. at 20 mm	d_4^{20}	n_D^{20}	MR_D	
				Found	Calc.
	101-101.5°	0.9777	1.4594	47.08	47.37
	137.5-138°	1.1050	1.4806	52.27	52.24
	113.5-114	0.9668	1.4608	51.70	51.99

Table 3 shows that the acetates have higher boiling points, higher specific gravities, and much lower refractive indexes than the alcohols. The odor of the acetates is fragrant and strong.

Oxidizing the secondary alcohols with a chromic acid mixture yields hydroaromatic ketones that are the same as those obtainable by condensing the respective dienes with methyl vinyl ketone.

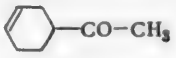
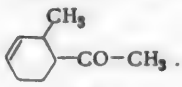
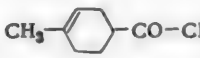
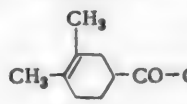
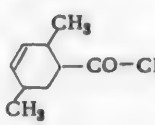
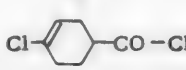
We secured tertiary alcohols by using the hydroaromatic ketones produced by condensing divinyl, piperylene, diisopropenyl, dipropenyl, and chloroprene with methyl vinyl ketone.

The formulas and constants of these ketones are given in Table 4. All these ketones, with the exception of the second and the fifth ones, have been described in previous papers.

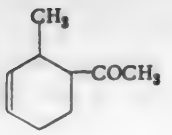
The structure of the condensation products of methyl vinyl ketone and the symmetrical dienes is not subect to any doubt. We might expect two isomeric hydroaromatic ketones to be formed when methyl vinyl ketone is condensed with piperylene and isoprene: (see following page).

The choice of the first (IIIa) and third (IVa) formulas, respectively, for these ketones was based upon the fact that the substance isolated proved to be the same as the ketones produced by oxidizing methyl-(2-methylcyclohexen-3-yl)- and methyl-(4-methylcyclohexen-3-yl)-carbinols, the structures of which have been established beyond any doubt.

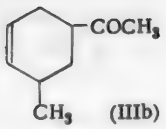
TABLE 4

Formula	B.p. at 20 mm	d_4^{20}	n_D^{20}	MR_D	
				Found	Calc.
	77.5-78.5°	0.9580	1.4698	36.15	36.49
	85-86	0.9387	1.4682	41.18	41.01
	91-91.5	0.9373	1.4706	40.94	41.01
	106.5-107	0.9374	1.4784	45.64	45.62
	100-102	0.9359	1.4732	45.72	45.62
	120-120.5	1.1216	1.4972	41.38	41.35

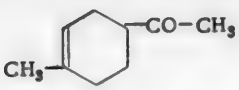
The structure of the condensation product of methyl vinyl ketone and chloroprene has not been established, though we may confidently assign it the formula given in the table, since alkyl vinyl ketones usually yield "para" products when reacted with chloroprene [12].



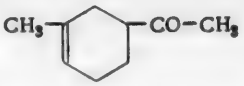
(IIIa)



(IIIb)



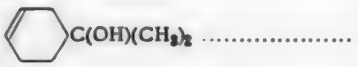
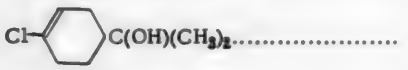
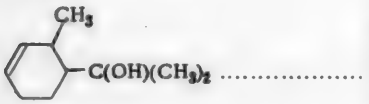
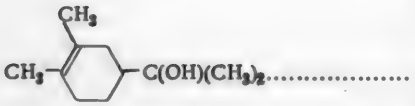
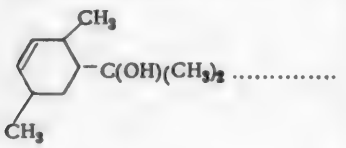
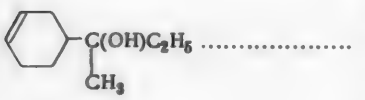
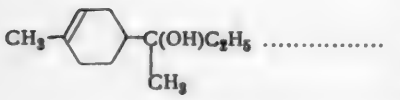
(IVa)



(IVb)

The reaction of CH_3MgI and C_2H_5MgI under the usual conditions with the ketones listed in the table yielded *a*-terpineol and several of its isomers, homologs, and analogs. The constants of the substances synthesized are collated in Table 5 with the findings of other researchers for these substances, insofar as these figures are to be found in the literature.

TABLE 5

Formula	Boiling point	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calculated	Reference
	95.5-96° (20 mm)	0.9479	1.4824	42.21	42.62	
	132-133° (20 mm)	1.0960	1.5038	47.17	47.47	
	102-103° (20 mm)	0.9405	1.4838	46.90	47.24	
	110-112° (30 mm)	0.9404	1.4792	46.53	47.24	[13]
	109.5-110° (20 mm)	0.9344	1.4830	47.17	47.24	
	120-122° (30 mm)	0.9350	1.4831	47.17	47.24	[14]
	121-121.5° (20 mm)	0.9370	1.4882	51.76	51.86	
	111.5-112.5 (20 mm)	0.9367	1.4844	51.30	51.86	
	108-109 (20 mm)	0.9483	1.4852	46.65	47.24	
	120-121° (20 mm)	0.9377	1.4850	51.30	51.86	
	235-237° (760 mm)	0.9390	1.4850	51.28	51.86	[14]

Dimethyl-(2-methylcyclohexen-3-yl)-carbinol was previously synthesized by reacting CH_3MgI with the ethyl ester of 2-methylcyclohexene-3-carboxylic acid. *a*-Terpineol has been synthesized in many ways, including the action of CH_3MgI upon 4-methylacetylcyclohexene-3 [14].

The action of C_2H_5MgI upon this ketone likewise yielded methylethyl-(4-methylcyclohexen-3-yl)-carbinol [14]. These syntheses were effected by Wallach. Wallach thus had in mind the possibility of synthesizing terpene alcohols from hydroaromatic ketones, but the relative inaccessibility of these ketones at that time did not

permit of the extensive utilization of this method. There is practically no difference between the constants of the tertiary alcohols determined by us and by previous research workers.

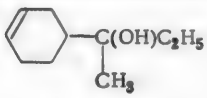
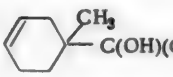
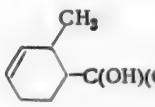
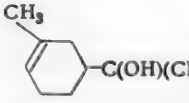
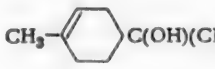
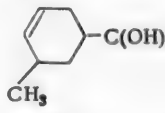
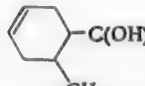
Dimethyl-(3,4-dimethylcyclohexen-3-yl)-carbinol crystallized in storage. The m.p. of this substance was 38-42° before recrystallization.

All the substances listed in Table 5 possess various shades of a flower fragrance.

Our work on the synthesis of tertiary alcohols from the respective ketones has disclosed all the isomers of α-terpineol that differ in the position of the methyl group, with the sole exception of dimethyl-(1-methylcyclohexen-3-yl)-carbinol. We secured this last isomer by reacting CH_3MgI with the condensation product of divinyl and a methyl methacrylate – the methyl ester of 1-methylcyclohexene-3-carboxylic acid.

Comparing the properties of all these isomers yields interesting conclusions concerning the change in their properties with a shift in the position of the methyl group. We see from Table 6 that as the radicals approach each other the boiling point drops, while the specific gravity and the refractive index increase. The sharp increase

TABLE 6

Formula	Boiling point	d_4^{20}	n_D^{20}	MR_D		Reference
				Found	Calculated	
	108-109° (20 mm)	0.9483	1.4852	46.65	47.24	–
	103.5-104 (20 mm)	0.9619	1.4912	46.46	47.24	–
	102-103 (20 mm)	0.9405	1.4838	46.90	47.24	–
	106-107 (20 mm)	0.9359	1.4775(α)	46.61(α)	46.99(α)	[15]
	109.5-110 (20 mm)	0.9344	1.4830	47.14	47.24	–
	104-105 (20 mm)	–	–	–	–	[16]
	110 (30 mm)	–	–	–	–	[17]

in the last two variables in compounds in whose molecules the two radicals are attached to the same carbon atom is worthy of note. The agreement between the experimental and the calculated values of the molecular refraction is best in the compounds with the substituents in the "para" position.

It is also of interest that all the isomers of α-terpineol at our disposal had different odors. The odor of the first substance (Table 6) reminds one of the odor of peppermint. The second substance has a strong camphor odor; at higher concentrations the vapor of this substance irritates the mucous membrane of the eye. The odor of the third substance is like that of the fourth – like α-terpineol – but is weaker and less pleasant. As we know, α-terpineol has a fragrant floral odor (lilac).

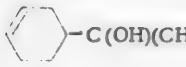
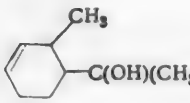
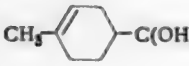
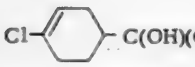
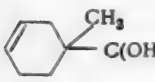
We investigated the following chemical properties of the tertiary alcohols we hyd synthesized: the behavior with bromine and acetic anhydride and their dehydration. Bromination of the dimethylcyclohexenylcarbinol

yielded crystalline (m.p. 87°) and liquid dibromides. Boiling the dibromide of dimethyl-(2-methylcyclohexen-3-yl)-carbinol in an acetic acid solution yielded o-cymene. Acetic anhydride causes dehydration of the alcohols even in the cold when a drop of H_2SO_4 is present.

We dehydrated the tertiary alcohols in various ways: 1) by heating with acetic anhydride; 2) by distilling over P_2O_5; and 3) by distilling with a 5% solution of oxalic acid.

We did not determine the structure of the hydrocarbons synthesized. Mixtures of the two possible isomers were apparently secured in every case but the last one. The constants of the hydrocarbons are given in Table 7.

TABLE 7

Initial alcohol	Constants of dehydration products					Dehydration method
	Boiling point	d_4^{20}	n_D^{20}	MR_D		
				Found	Calculated	
	151-155° (760 mm)	0.8467	1.4774	40.80	40.63	1
	172-174 (760 mm)	0.8544	1.4785	45.18	45.25	1
	176-177 (760 mm)	0.8498	1.4830	45.78	45.25	1
	94.5-95.5 (20 mm)	1.0169	1.5014	45.95	45.50	2
	63-64 (20 mm)	0.8574	1.4768	44.88	45.25	3

The first and last substances have aromatic odors. The odor of the second substance is like that of dipentene.

When we compare the constants of the hydrocarbons synthesized from α-terpineol with those of the possible dehydration products – dipentene and terpinolene, we may conclude that the substance consists of both of these products, with the first one predominating.

It might be expected that dehydration of dimethyl-(1-methylcyclohexen-3-yl)-carbinol would result in formation of only one substance, namely, 1-methyl-1-isopropenylcyclohexene-3. We are the first to have described this substance.

The products of the dehydration of the tertiary alcohols were dehydrogenated over palladium, the second, third, and fourth of these substances yielding the corresponding aromatic hydrocarbons. The fourth substance, for example, loses its halogen atom in dehydrogenation, yielding cumene. When the product of the dehydration of dimethyl-(1-methylcyclohexen-3-yl)-carbinol is passed over palladium under the same conditions, no hydrogen is split off, which is in conformity with its supposed structure.

EXPERIMENTAL

1. Preparation of the initial hydroaromatic aldehydes and ketones. The dienes were condensed with acrolein and methyl vinyl ketone in open glass ampoules inside a steel autoclave at 120-140°. Heating was continued for 6 hours. The yield of hydroaromatic aldehydes and ketones totaled 75-80% of the initial aldehyde or ketone, as a rule. A considerable excess of piperylene and hexadiene-2,4 was used, since only the trans form of these hydrocarbons enters into the reaction.

The constants of the substances synthesized are listed in Table 1 and 4. It should be noted that the boiling points of the hydroaromatic ketones as published in an earlier paper by one of the present authors are somewhat high (by some 2-3°), evidently due to incorrect readings of the vacuum-meter.

The previously unknown p-nitrophenylhydrazone of the piperylene ketone, with a m.p. of 143-144°, has been prepared.

The condensation product of acrolein and isoprene was oxidized under the following conditions. 6.2 g of the aldehyde was added in small portions, with vigorous agitation, to an aqueous suspension of silver oxide, prepared from 16.9 g of $AgNO_3$. After the mixture had been heated for an hour on a water bath, ammonia was added, the precipitated silver was filtered out, the solution acidulated with H_2SO_4, and the organic acid extracted with ether. Driving off the ether yielded 5.5 g of a crystalline acid, which had a m.p. of 85° after having been washed with petroleum ether (0.5 g loss) and 98° after recrystallization from water; this is the figure for 4-methylcyclohexene-3-carboxylic acid [18]. The mixed melting point of the substance synthesized and known 4-methylcyclohexene-3-carboxylic acid exhibited no change.

2. Synthesis and properties of the secondary alcohols. A solution of 0.2 mole of the hydroaromatic aldehyde in 100 ml of ether was added with chilling and mechanical stirring to a solution of an organomagnesium compound, prepared from 0.2 gram-atom of magnesium and 0.22 mole of methyl or ethyl iodide in 200 ml of absolute ether. After the ether solution had stood for 1 hour and been heated for 1.5 hours, it was poured into a flask containing a solution of ammonium chloride and pieces of ice. The ether solution of the secondary alcohol was dried with calcined Na_2SO_4 and then distilled. The yield of alcohols was 78-82%, based on the aldehyde. The constants of the alcohols synthesized are given in Table 2. We cite the analytical data (Table 8).

Methyl-(4-chlorocyclohexen-3-yl)-carbinol. 0.1587 g substance: 0.1494 g AgCl. Found %: Cl 23.26. $C_8H_{13}OCl$. Calculated %: Cl 22.07.

The alcohols were acetylated as follows: One drop of conc. H_2SO_4 was added to a mixture of 0.1 mole of the alcohol and 0.15 mole of acetic anhydride, after which the mixture was agitated and chilled with a jet of water to keep the temperature from rising above 50°. Then the mixture was diluted with water, the resulting oil being washed with water and a soda solution and then distilled. The constants of the resulting acetates are given in Table 3. We cite the analytical findings (Table 9).

Acetate of methyl-(4-chlorocyclohexen-3-yl)-carbinol. 0.1512 g substance: 0.1084 g AgCl. Found %: Cl 17.72. $C_{10}H_{15}O_2Cl$. Calculated %: Cl 17.49.

The alcohols were oxidized as follows. 0.02 mole of sodium dichromate was added to a solution of 0.05 mole of the alcohol in 30 ml of acetic acid, and then 50% H_2SO_4 was added drop by drop (100% excess) with cooling (to 15-20°) and mechanical stirring. After the reaction was over, the solution was diluted and neutralized with soda, and the ketone was extracted with ether. The ketone remaining after the ether had been driven off on a water bath was converted into a semicarbazone (to separate it from the unreacted alcohol) and then recovered from the semicarbazone, washed on the filter with ether, by distillation with a 5% solution of H_2SO_4. The yields of the pure ketone averaged 20-30%. In this way methyl-(2-methylcyclohexen-3-yl)-carbinol yielded 2-methylacetylcyclohexene-3, with a b.p. 85-86° at 20 mm; n_D^{20} 1.4688. The melting point of the p-nitrophenylhydrazone was 142-144°. All these figures correspond exactly with those found for the ketone produced by condensing piperylene with methyl vinyl ketone.

The methyl-(4-methylcyclohexen-3-yl)-carbinol yielded 4-methylacetylcyclohexene-3 with a b.p. of 90-92° at 20 mm and n_D^{20} 1.4710. The melting point of the semicarbazone was 150-151°, and that of the p-nitrophenylhydrazone was 166-167°, which again agrees with the figures given in the literature.

Oxidation of ethyl-(cyclohexen-3-yl)-carbinol yielded the hitherto unknown propionylcyclohexene-3. B.p. 90-90.5° at 20 mm, d_4^{20} 0.9405, n_D^{20} 1.4700, MR_D 40.97. $C_9H_{14}O$; calculated 41.11.

0.1384 g substance: 0.3957 g CO_2; 0.1284 g H_2O. Found %: C 78.02; H 10.38. $C_9H_{14}O$. Calculated %: C 78.21; H 10.21.

It was difficult to form the semicarbazone of this ketone (precipitation took 3 days). M.p. 138°. It was recrystallized from aqueous alcohol.

We were unable to secure crystalline products by adding nitrosyl chloride to the first and third substances (Table 3) under ordinary conditions.

The alcohols were brominated in a chilled chloroform solution with a calculated quantity of a chloroform solution of bromine. The solvent was driven off in vacuo at room temperature. The first, second, third, and fifth substances (Table 3) were brominated. In every instance we secured a thick oil, which was not analyzed further.

TABLE 8

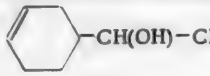
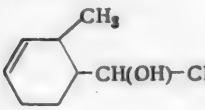
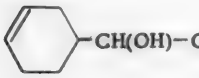
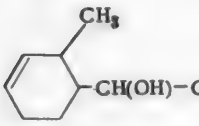
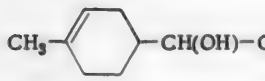
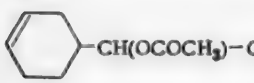
Substance	g	CO_2 g	H_2O g	Found % C	Found % H	Formula	Calculated % C	Calculated % H
	0.1713	0.4816	0.1701	76.72	11.11	$C_8H_{14}O$	76.13	11.18
	0.1687	0.4781	0.1752	77.33	11.62	$C_9H_{16}O$	77.08	11.50
	0.1379	0.3901	0.1355	77.20	11.50	$C_9H_{16}O$	77.08	11.50
	0.1733	0.4958	0.1786	78.07	11.53	$C_{10}H_{18}O$	77.86	11.76
	0.1641	0.4694	0.1634	78.06	11.14	$C_{10}H_{18}O$	77.86	11.76

TABLE 9

Substance	g	CO_2 g	H_2O g	Found % C	Found % H	Formula	Calculated % C	Calculated % H
	0.1546	0.4010	0.1313	70.78	9.28	$C_{10}H_{16}O_2$	71.39	9.58
	0.1342	0.3553	0.1186	72.25	9.88	$C_{11}H_{18}O_2$	72.10	9.90

3. Synthesis and properties of the tertiary alcohols. The tertiary alcohols were synthesized under the same conditions as those used for the secondary alcohols, the yields being somewhat lower in this case: 60-70%.

A tertiary alcohol with two radicals attached to the same carbon atom was synthesized by reacting CH_3MgI in ether with the condensation product of divinyl and methyl methacrylate, which was described in one of our preceding reports [19]. The yield was 89%.

The constants of the tertiary alcohols are given in Table 5. We give below the analytical findings for the substance synthesized for the first time (Table 10).

Bromination of the first and fourth substances listed in Table 5 under the conditions specified in the preceding section yielded viscous oils. Crystals with a m.p. of 87° settled out when the dibromide of the first substance was allowed to stand for a long time. (Found %: Br 53.78).

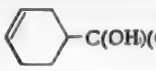
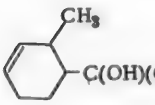
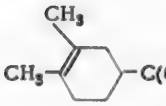
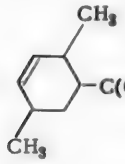
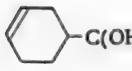
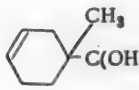
The action of nitrosyl chloride upon α-terpineol yielded a crystalline product with a m.p. of 103°, described in the literature.

Dimethyl-(4-chlorocyclohexen-3-yl)-carbinol. 0.1440 g substance: 0.1206 g AgCl. Found %: Cl 20.72. $C_9H_{15}OCl$. Calculated %: Cl 20.30.

Dimethyl-(cyclohexen-3-yl)-carbinol does not yield a crystalline product whenreacted with nitrosyl chloride.

3.6 g of dimethyl-(2-methylcyclohexen-3-yl)-carbinol was brominated (4 g of bromine in 25 ml of acetic acid). After the solution had boiled for 6 hours (until no more hydrogen bromide was evolved), it

TABLE 10

Substance	g	CO_2 g	H_2O g	Found % C	Found % H	Formula	Calculated % C	Calculated % H
	0.1908	0.5375	0.1916	76.88	11.24	$C_9H_{16}O$	77.08	11.50
	0.1871	0.5321	0.1935	77.61	11.57	$C_{10}H_{18}O$	77.86	11.76
	0.1657	0.4751	0.1674	78.25	11.31	$C_{11}H_{20}O$	78.51	11.98
	0.1453	0.4157	0.1379	78.08	10.64	$C_{11}H_{20}O$	78.51	11.98
	0.1618	0.4617	0.1703	77.87	11.78	$C_{10}H_{18}O$	77.86	11.76
	0.1353	0.3863	0.1442	77.98	11.92	$C_{10}H_{18}O$	77.86	11.76

was neutralized and distilled with steam. This yielded 1.5 g of o-cymene, with a b.p. of 175-176°; d_4^{20} 0.8770, n_D^{20} 1.4985. The figures given in the literature [20]: B.p. 175°, d_4^{20} 0.876, n_D^{20} 1.5000.

In most instances the tertiary alcohols were dehydrated by heating the alcohol to 200° for 6 hours in sealed tubes with a 50% excess of acetic anhydride. The yield of hydrocarbons was 85-90%. The chlorine-substituted alcohol was dehydrated by distillation over P_2O_5 in vacuo. The chloride yield was 70%. Dimethyl-(1-methylcyclohexen-3-yl)-carbinol was dehydrated by distilling it with a 5% solution of oxalic acid. The hydrocarbon yield was 80%. The constants of the dehydration products are given in Table 7. The analytical findings for the substances synthesized for the first time are given below (Table 11).

Dehydration product of dimethyl-(4-chlorocyclohexen-3-yl)-carbinol: 0.1592 g substance: 0.1435 g AgCl. Found %: Cl 22.30. $C_9H_{15}Cl$. Calculated %: Cl 22.63.

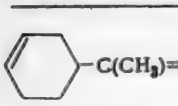
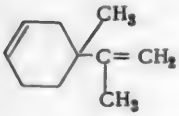
Dehydrogenation of the third substance in Table 7 in a single pass over palladinized asbestos at 300° yielded a condensate that did not decolorize bromine water, with a b.p. of 176-177°; d_4^{20} 0.8530, n_D^{20} 1.4882. The following constants are given in the literature for p-cymene [20] b.p. 177°, d_4^{20} 0.8570, n_D^{20} 1.4904.

When the dehydration product of dimethyl-(4-chlorocyclohexen-3-yl)-carbinol was passed over the catalyst under the same conditions, the hydrohalide was split out and 65% of cumene was produced. B.p. 151-153°, d_4^{20} 0.8613, n_D^{20} 1.4918. Figures in the literature [21]: B.p. 152.5°, d_4^{20} 1.8640, n_D^{15} 1.4947.

SUMMARY

1. Various findings relating to the condensation of dienes with acrolein and methyl vinyl ketone have been defined more accurately; in particular, the structure of the condensation products of isoprene with acrolein and methyl vinyl ketone and of piperylene with the last-named substance has been established.

TABLE 11

Substance	g	CO_2 g	H_2O g	Found % C	Found % H	Formula	Calculated % C	Calculated % H
	0.1063	0.3460	0.1103	88.82	11.61	C_9H_{14}	88.45	11.55
	0.1183	0.3836	0.1256	88.49	11.88	$C_{10}H_{16}$	88.16	11.84

2. The action of methylmagnesium iodide and ethylmagnesium iodide upon hydroaromatic aldehydes and ketones — products of the condensation of dienes with acrolein and methyl vinyl ketone — has yielded several secondary and tertiary hydroaromatic alcohols not described previously in the literature: the isomers, homologs, and analogs of α-terpineol.

3. Dimethyl-(1-methylcyclohexen-3-yl)-carbinol, not described previously in the literature, has been synthesized by the action of methylmagnesium iodide upon the condensation product of divinyl and methyl methacrylate.

4. Several acetates of the secondary alcohols have been synthesized by acetylating these alcohols with acetic anhydride.

5. The respective hydroaromatic ketones, particularly the hitherto undescribed propionylcyclohexene-3, have been synthesized by oxidizing the secondary alcohols with a chromic acid mixture.

6. Several hydroaromatic hydrocarbons, especially 1-methyl-1-isopropenylcyclohexene-3, not previously described in the literature, have been synthesized by dehydrating the tertiary alcohols. The dehydrogenation of some of the synthesized hydrocarbons over palladium has been explored.

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THE CONFIGURATION OF THE CRYSTALLINE BROMIDES OF BUTADIENE

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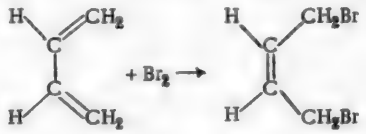
As we know, butadiene reacts with bromine to form two tetrabromides, with m.p. of 39 and 118°, and two dibromides, one of which is a liquid and the other is crystalline, with a m.p. of 53°. In the past, the liquid dibromide was assigned the structure of cis-1,4-dibromobutene-2, with the crystalline dibromide, m.p. 53°, assigned the configuration of trans-1,4-dibromobutene-2 [1]. It was later demonstrated that the liquid dibromide is a product of the addition of bromine to butadiene at the 3 and 4 positions. Hence, it is 3,4-dibromobutene-1 [2].

A study has been made of the transformation of the crystalline dibromide into erythrites and tetrabromobutanes in order to determine its configuration. Examination of the literature on the subject indicates that various groups are added at the double bond of the dibromide partly in the cis position and partly in the trans position [3]. Hence, these findings do not provide an unequivocal answer concerning the configuration of the dibromide.

In the present research we have investigated the Raman spectra of the butadiene bromides. Two frequencies for the C—Br bond, 593 and 628 cm^{-1}, and a frequency for the double bond, 1655 cm^{-1}, have been found in the spectrum of the crystalline dibromide with a m.p. of 53°. The 593 and 628 cm^{-1} frequencies refer to the $-CH_2Br$ group. The double-bond frequency value provides an unequivocal answer to the problem of the configuration of the crystalline dibromide, which can only be a cis form. The frequency of the C=C bond would have to be 1670 to 1680 cm^{-1} for the trans form.

These findings indicate that butadiene enters into reaction with bromine in its "bent" form, resulting in the formation of the cis-dibromide.



Turning to the problem of the configuration of the butadiene tetrabromides, we must point out that the two known crystalline forms represent the possible geometrical isomers. One of them is a meso form, while the other is a dl form.

Investigation of the Raman spectra of the tetrabromides showed that the tetrabromide with a m.p. of 39° contains four C—Br bond frequencies, 568, 608, 638, and 673 cm^{-1}, while only two frequencies were found for the C—Br bond, 568 and 598 cm^{-1}, in the spectrum of the tetrabromide with a m.p. of 118°. The 50% drop in the number of C—Br bond frequencies in the high-melting tetrabromide may be due to the presence of an axis of symmetry in its molecule. This is conceivable for the dl form, but cannot occur with the meso form.

It follows from the foregoing that the high-melting tetrabromide of butadiene has a dl configuration. The low-melting tetrabromide is the meso form.

The spectra of all the crystalline bromides were photographed in their carbon tetrachloride and acetone solutions. The solutions used were of approximately equal concentration.

SUMMARY

1. The butadiene dibromide with a m.p. of 53° is cis-1,4-dibromobutene-2.

2. The butadiene tetrabromide with a m.p. of 39° is the meso form of 1,2,3,4-tetrabromobutane.

3. The butadiene tetrabromide with a m.p. of 118° is the dl form of 1,2,3,4-tetrabromobutane.

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THE BROMINATION AND IODOXATION OF 1,1-DIALKYLBUTADIENES-1,3. VIII.

V.I.Esafov

It has been shown in our previous report [1] that dienes of the $CH_2=\underset{\underset{R}{|}}{C}-CH=CH_2$ and $CH_2=\underset{\underset{R}{|}}{C}-\underset{\underset{R}{|}}{C}=CH_2$ types are examples of departures from the M.D.Lvov-D.V.Tishchenko rule, no matter whether they have one or two quaternary carbon atoms at the double bonds. Owing to the appreciable conjugation of the double bonds they add bromine principally at the 1,4-position during gentle bromination. We found it necessary to trace the course of the bromination and iodoxation reactions of dienes of the 1,1-dialkylbutadiene-1,3 type, the molecules of which are, according to the electronic theory, more polar than divinyl, which ought to promote the reaction at the 1,4 position. Study of the bromination and iodoxation of 1,1-dimethylbutadiene-1,3 and 1-methyl-1-ethylbutadiene-1,3 has shown, however, that, in contrast to the symmetrically disubstituted butadienes, viz.: hexadiene-2,4 [2] and diisopropenyl, the first of these compounds is brominated more completely and with the evolution of considerable HBr, provided all other conditions remain the same.

These new findings support the rule derived empirically [1]: that the less symmetrical the position of conjugated double bonds in a system, the greater the effect of radicals upon the degree of conjugation of these bonds. On the other hand, we observed that the 1,1-dialkylbutadienes-1,3 react readily with maleic anhydride. Thus, 1,1-dialkylbutadienes-1,3 exhibit perceptible autonomy of their double bonds during bromination and iodoxation, whereas they react like conjugated systems with maleic anhydride. It seems to us that these facts are weighty arguments against any stereotyped application of present-day hypotheses founded upon the electronic theory in explaining the reactions of organic compounds.

In support of this assertion we may cite the findings of D.V.Tishchenko [3], who found that the chlorination of aliphatic halogenated derivatives proceeds contrary to the concept of the so-called alternating effect adopted by some chemists [4].

Dienes of the 1,1-dialkylbutadiene-1,3 type were first produced in A.M.Zaitsev's laboratory [5] by dehydrating dialkylallylcarbinols with dilute sulfuric acid or by splitting out molecules of hydrogen chloride from the chlorohydrins of the carbinols. Reformatsky [6], however, assigned them the structure of dienes with independent double bonds on the basis of his study of their oxidation products with a chromic acid mixture. Slobodin [7], on the contrary, has shown that the dehydration of dialkylallylcarbinols* with dilute sulfuric acid proceeds in two directions, dienes with conjugated double bonds being principally formed, whereas diisopropylallylcarbinol is chiefly dehydrated to 2-methyl-3-isopropylhexadiene-2,5. Petrov and his students [8] have shown that dehydrating methylhexylallylcarbinol over Al_2O_3 at 290-300° results in 72% of the theoretical yield of 4-methyldecadiene-1,4, the isomeric 4-methyldecadiene-1,3 being present as an impurity. Not so long ago Favorskaya and Fridman [9] discovered the interesting fact that methylphenyl- and diphenylallylcarbinols undergo ketonic cleavage when heated with 25% H_2SO_4. Under these same conditions dimethylallylcarbinol yielded no acetone at all, on the other hand, while methylethylallylcarbinol [10] mainly underwent isomerization to a primary alcohol with the structure of $(CH_3)_2C=CH-CH_2CH_2OH$, while being dehydrated to dienes.

In view of the fact that the catalytic dehydration of dialkylallylcarbinols results in dienes with independent double bonds, while the action of sulfuric acid produces a low yield of hydrocarbons, as Slobodin has indicated, we utilized the dehydration of tertiary α,β-unsaturated carbinols with iodine to secure 1,1-dialkylbutadienes-1,3. We found that the reaction rate depends upon the amount of iodine used in the reaction, the carbinol reacting with it and liberating heat. In view of the fact that dimethylallylcarbinol, for example, is fairly stable thermally, while its decomposition sets in at the boiling point when iodine is present, it must be assumed that it is not the carbinol proper that decomposes but rather its oxonium compounds with the iodine.

* With a greater or equal degree of hydrogenation of the carbon atoms in the alkyl groups adjacent to the carbinol group, as compared with the allyl radical.

When a compound of this sort is heated it not only turns 1,1-dimethylallylcarbinol (and to a lesser degree methylallylcarbinol) into dienes, but is also decomposed at the point where the allyl radical is connected to the carbinol carbon atom.* Thus, we can say that under suitable conditions and when acted upon by certain chemical agents, tertiary carbinols containing an allyl radical can be cleaved at the least stable of their C—C bonds: $RRC(OH)-CH_2CH=CH_2$, this being a general property of theirs.

EXPERIMENTAL

1. Syntheses of dialkylallylcarbinols.** In accordance with Yavorsky's prescription [11], the magnesium used for these reactions was first pickled for 4 hours in allyl bromide. We used 0.5 moles of the ketones and the allyl bromide and 150 ml of absolute ether in synthesizing the carbinols. The reactions were carried out in our apparatus [1], with the stirrer in continuous operation. The reaction flask was chilled with snow at the very outset of the synthesis until the violent reaction ceased. The ketones and the allyl bromide were added separately by dropping during the course of 4 hours, after which the mass was stirred for another 1 hour. After the mass had been allowed to stand at rest for an hour, the reaction product was decomposed with ice and then with aqueous ammonia. The yield of dimethylallylcarbinol averaged 43.2% of the theoretical; its b.p. was 117-118° (732 mm); d_4^{20} 0.8308 n_D^{20} 1.4300 MR_D 31 12 calculated 31 08.

The yield of methylethylallylcarbinol was 42.9% of the theoretical, its b.p. being 138-139° (735 mm); d_4^{20} 0.8323; n_D^{20} 1.4310; MR_D 35.73; calculated 35.70.

The iodine numbers of the carbinols were determined by the MacIlhinney method, which yielded fairly dependable results (Table 1).

2. Experiments on the dehydration of dialkylallylcarbinols. a) No dehydration occurred when the vapor of 10 g of dimethylallylcarbinol was passed through a glass coil heated to 290° for 20 minutes.

b) Dehydrating dimethylallylcarbinol with sulfanilic acid yielded only little of the dienes. In view of the fact that dehydrating dialkylallylcarbinol with either sulfanilic acid or dilute sulfuric acid [7] produced low yields of dienes, we proceeded to test dehydrating the carbinols in the presence of iodine.

c) When dimethylallylcarbinol was distilled rapidly with a crystal of iodine, the dehydration was negligible.

d) Subsequent dehydration experiments were performed in the following apparatus, designed to increase the time during which the carbinol was in contact with the iodine. A round-bottomed flask was connected to a water trap of a Dean-Stark apparatus. A 70-cm herringbone dephlegmator, terminated with a thermometer, was placed in the trap. The dephlegmator was connected to a condenser, the end of which was connected via an adapter with a gas outlet tube to the collector and to a gasometer.

When 26 g of dimethylallylcarbinol was boiled with 0.02 g of iodine, the first thing noticed was the evolution of gas, 46.3 ml of it (at 20° and 740 mm) being collected, after which the liquid began to distil slowly, the reading of the thermometer in the dephlegmator not rising above 80°. The distillation of the liquid fell off after 1.5 hours of heating. After 2 hours of heating, another 0.2 g of iodine was placed in the flask, 50 ml more of gas being evolved and the liquid distilling rapidly, distillation coming to an end after 1 hour had elapsed. These tests show that the extent of dehydration of this carbinol depends upon the quantity of iodine used as well as upon the increase of the time of contact with the iodine.

The gas was found to contain 2.2% by volume of propylene. The liquid distillate was treated with 15 ml of water to eliminate the water-soluble substances. The first distillation of the hydrocarbon layer yielded the following fractions: 1) 56-65° — 2.9 g; 2) 65-75° — 7.5 g; and 3) 75-76° — 3.5 g.

The wash-water liquid was mixed with the aqueous liquid in the trap (see below). The residue left in the flask and the 4 g of liquid organic product collected in the trap were treated with a potassium iodide solution to remove the iodine, washed with water, and dried with anhydrous sodium sulfate (see below).

e) The experiment was repeated, adding 1 g of sublimed anhydrous iodine to 26 g of the dimethylallylcarbinol; intensive local heating, with crepitation, being observed. When the mixture was boiled, 140 ml

* We observed this fact in 1948 in association with O.G.Boyarshinova.

** In association with O.G.Boyarshinova and L.P.Lebedeva.

TABLE 1

Bromination of Dialkylallylcarbinols and of Their Dehydration Products

Test No.	Wt. g	Ml of Br−CCl_4 solution	Ml of 0.1 N H_2SO_4 solution: Used to titrate excess halogen	Ml of 0.1 N H_2SO_4 solution: Equiv. consumption of I for sample	Ml of 0.1 N H_2SO_4 solution: Used to titrate I in HI	Overall iodine number	Iodine number of splitting	Iodine number proper	Halogen converted into HBr as % of total halogen consumption
	Dimethylallylcarbinol						By theory	253.61	
1	0.0852	9.0	48.58	17.52	0.47	261.01	14.0	247.01	
2	0.0766	9.0	50.84	15.26	0.41	252.86	13.58	239.28	
	Methylethylallylcarbinol						By theory	222.28	
1	0.0642	6.1	27.40	11.40	0.39	225.39	15.42	209.97	
2	0.0672	6.1	26.62	12.80	0.39	230.06	14.58	215.48	
	Hydrocarbon with b.p. of 56-59°						By theory	618.56	
1	0.1185	7.3	0.14	30.14	1.27	322.84	27.20	295.64	4.21
2	0.1116	13.0	13.14	40.78	2.06	463.81	46.85	416.96	5.05
	1,1-Dimethylbutadiene-1,3						By theory	618.56	
1	0.1608	9.4	0.02	36.86	2.59	290.96	40.88	250.08	7.02
2	0.1023	12.1	11.38	36.10	4.22	447.91	104.72	343.19	11.66
	Hydrocarbon with b.p. of 90-92°						By theory	528.34	
1	0.0894	4.5	0.08	18.48	0.83	262.37	23.56	238.81	4.49
2	0.0614	6.2	8.90	16.68	0.63	344.82	26.04	318.78	3.77
	Hydrocarbon with b.p. of 108-110°						By theory	528.34	
1	0.0926	4.8	0.04	19.68	0.48	269.76	13.15	256.61	2.43
2	0.0768	8.0	15.12	17.76	0.80	293.52	26.44	267.08	4.50

of gas (at 20° and 740 mm) was first given off, and then the liquid distilled rapidly. The dehydration process was completed within 15 minutes. The subsequent operations were the same as in Experiment d. The residue in the reaction flask and the trap totaled 7.5 g. The first fractionation of the liquid distillate yielded the following fractions: 1) 56-65° − 1.6 g; 2) 65-75° − 5.2 g; 3) 75-100° − 1.7 g; and above 100° − 2.7 g.

Comparison of the results of experiments d and e indicates that increasing the amount of iodine placed in the reaction accelerates the dehydration of the carbinol, but also increases the quantity of by-products.

The aqueous wash liquids of the two experiments were combined, salted out with sodium chloride, and reduced to two-thirds of their volume by distillation. The distillate was a two-layer liquid, the lower, aqueous layer exhibiting an iodoform reaction, proving that acetone was present as the result of the decomposition of the dimethylallylcarbinol into acetone and propylene. This was likewise proved by the formation of acetone condensation products, contained in the carbinol decomposition residues. Fractionation of the residues of the two experiments yielded the following fractions: 1) up to 122° − 1.5 g; 2) 122-135° − 1.3 g; 3) 135-225° − 2 g; and 4) 5 g of a dark residue. The 122-135° and 135-225° fractions were each boiled for two hours with 6 ml of a 0.2 N solution of NaOH.

After this heating of the reaction products, the aqueous solutions were driven off, the distillates being filtered through moist filters and diluted to 10 ml with water, after which they were tested for acetone, the presence of which was demonstrated by an iodoform reaction as well as by a V.V.Chelintsev − Nikitin reaction [12].

Thus, the discovery of a negligible amount of gas, and particularly the finding of acetone and of its condensation products, proved that the dimethylallylcarbinol was cleaved at the C — C bond between the allyl radical and the carbinol carbon atom:

Further repeated fractionation of the combined hydrocarbon fractions at 745 mm yielded the following fractions: 1) 56-59° — 3.0 g; 2) 59-75° − 5.7 g; and 3) 75-76° − 6.8 g.

The hydrocarbon with a b.p. of 56-59° had d_4^{20} 0.7001; n_D^{20} 1.4029; MR_D 28.60. The hydrocarbon with

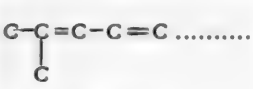
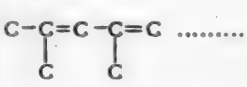
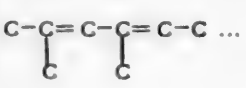
a b.p. of 75-76° had d_4^{20} 0.7196; n_D^{20} 1.4432; MR_D 30.25. $C_6H_{10}\bar{F}_2$. Calculated 28.974; the exaltation was +1.276.

Bromination of the hydrocarbon with a b.p. of 56-59° (see Table 1) (without using an excess of the bromine solution) indicated that the molecule had more than one double bond. Oxidizing the hydrocarbon with permanganate at 0° yielded acetone and formic acid. After the volatile acids had been driven off, we were unable to find any dibasic acids in the residue. These findings proved that the hydrocarbon with a b.p. of 56-59° contained 2-methylpentadiene-1,4 with a possible trace of diallyl.

Bromination of the hydrocarbon with a b.p. of 75-76° (Table 1) indicated that its double bonds had less autonomy than in its more highly substituted analog (Table 2), though its autonomy was high enough, compared to the symmetrically disubstituted butadienes-1,3.

TABLE 2

Comparison of the Bromination Data for Some Dienes

No.	Molecular carbon skeletons	At a quantity of $Br-CCl_4$ solution sufficient to saturate the double bonds completely	
		Overall iodine numbers, % of theoretical	Halogen converted into HBr, as % of total halogen consumption
1		72.2	11.6
2		76.2	17.0
3		81.7	24.1

The presence of conjugated double bonds in this hydrocarbon can be readily proved by its reaction with maleic anhydride dissolved in toluene. The reaction produces a yellow color, accompanied by the evolution of considerable heat. The ampoule was heated for 2 hours on a boiling water bath to complete the reaction. After the reaction product had been treated with alkali and the toluene had been driven off, the potassium salts were decomposed with dilute sulfuric acid. As the solution was chilled, 1,1-dimethylcyclohexen-2-dicarboxylic acid-5,6 crystallized out. Our findings agree with those of Slobodin [7], but contradict those of Gorin and his associates [13], who, referring to Farmer and Worren [14], state that 2-methylpentadiene-2,4 yields a yellowish amorphous mass (polymer product) when treated with maleic anhydride.

When the hydrocarbon with a b.p. of 75-76° was oxidized with permanganate at 0°, the neutral products contained acetone, and the volatile acids contained formic acid, 1.5 g of the hydrocarbon yielding 0.46 g of the acid. These findings indicate that the hydrocarbon with a b.p. of 75-76° is 1,1-dimethylbutadiene-1,3.

3 Experiments on dehydrating methylethylallylcarbinol in the presence of iodine. This hydrocarbon was dehydrated as we dehydrated the hydrocarbon of Experiment 2, using 0.2 g of anhydrous, sublimed iodine for 28.5 g of the carbinol. The whole process was completed within 25 minutes. The liquid distillate totaled 20.6 g, and the residue in the flask and the trap totaled 3.5 g. The aqueous liquid left after the distillate had been treated with water did not exhibit an iodoform reaction (after 20 minutes of standing). After the hydrocarbon layer had been dried with $CaCl_2$, it was repeatedly distilled (727 mm) over Na in a current of anhydrous CO_2. This yielded the following fractions: 1) up to 90° – 1 g; 2) 90-92° – 4.0 g; 3) 92-95° – 1.6 g; 4) 95-108° – 2.1 g; 5) 108-110° – 3.2 g; and a residue of 0.6 g. The hydrocarbon with a b.p. of 90-92° had d_4^{20} 0.7324; n_D^{20} 1.4180; MR_D 33.06. The hydrocarbon with b.p. 108-110° had d_4^{20} 0.7558; n_D^{20} 1.4523; MR_D 34.32. $C_7H_{12}\bar{F}_2$. calculated 33.59. The exaltation was 0.73. These hydrocarbons were brominated (Table 1), the hydrocarbon with a b.p. of 90-92° exhibiting more than one double bond in its molecule. On the other hand, the hydrocarbon with a b.p. of 108-110° was brominated like a diene, with appreciable conjugation of double bonds, differing sharply from 1,1-dimethylbutadiene-1,3, Iodoxation of the hydrocarbon with a b.p. of 108-110° is, however, fully like that of 1,1-dimethylbutadiene (Table 3) and is accompanied by even greater conversion of iodine into HI, as is typical of dienes with slight conjugation of double bonds.

Such differing behavior of the hydrocarbon with a b.p. of 108-110° in the bromination and iodoxation reactions deserved special investigation. In contrast to the hydrocarbon with a b.p. of 90-92°, that with a b.p. of 108-110° reacted with a solution of maleic anhydride in toluene, evolving considerable heat. We secured a high

TABLE 3

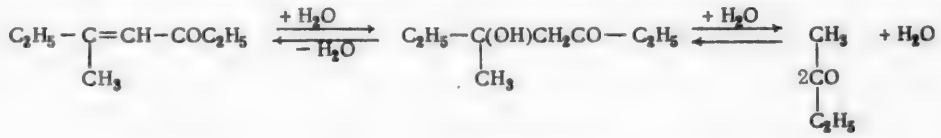
Iodoxation of Dienes

Test No.	Weight, grams	Ml of 0.1 N $Na_2S_2O_3$ solution			Iodine number	Per cent iodine converted into HI
		Used to titrate excess iodine	Equivalent consumption of I for the sample	Used to titrate iodine in HI		
	1,1-Dimethylbutadiene-1,3					
1	0.0812	9.96	18.90	9.60	295.44	50.78
2	0.1275	84.79	49.56	33.70	493.38	67.99
	Hydrocarbon with a b.p. of 108-110°					
1	0.0798	13.82	15.04	12.43	239.22	82.64
2	0.1438	84.70	49.55	41.32	438.25	83.22

yield of the supposed 1-methyl-1-ethylcyclohexene-2-dicarboxylic acid-5,6, with m.p. of 170°. Its Ag salt was produced by saturating the acid with silver carbonate and then evaporating the solution on a boiling water bath. Analysis of the Ag salt,* dried at 85°, yielded the following figures:

0.1743 g substance: 0.0836 g Ag. Found %: Ag 47.96. $C_{11}H_{14}O_4Ag_2$. Calculated %: Ag 50.66.

Study of its properties as well as the analogy of its behavior to that of the dimethyl- and methylethylallylcarbinols indicated that the hydrocarbon with a b.p. of 108-110° consisted chiefly of 1-methyl-1-ethylbutadiene-1,3. The dark residue left in the flask after the iodine had been removed and the remainder dried was fractionated. The fraction with a b.p. of 155-170° displayed a positive iodoform reaction, indicating that it contained the condensation products of methyl ethyl ketone in the most likely form of 3-methylhepten-3-one-5. Though this latter ketone was an ethyl ketone, as an α,β-unsaturated ketone it was hydrolytically cleaved in the presence of a 1 N NaOH solution, yielding methyl ethyl ketone, which was the basis for the positive iodoform reaction:



SUMMARY

1. It has been shown that dialkylallylcarbinols are dehydrated in the presence of iodine in two ways, yielding dienes with independent as well as conjugated double bonds. A decrease in the degree of hydrogenation of the alkyl groups attached to the carbinol carbon atoms lowers the yield of the latter dienes.

2. It has been shown that, in contrast to diisopropenyl and hexadiene-2,4, the double bonds are less conjugated in 1,1-dimethylbutadiene-1,3, so that its bromination and iodoxation reactions are more complete.

3. It has been shown that the ability of tertiary alcohols containing an allyl radical to be cleaved at the bond between the allyl radical and the carbinol carbon atom is a general property of these alcohols.

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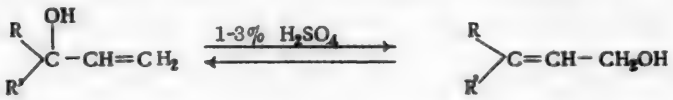
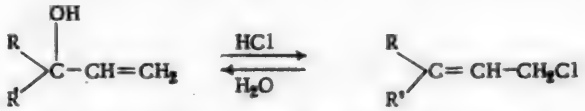
135. REARRANGEMENT OF AN ALLYLIC SYSTEM. V. EXCHANGE REACTIONS OF γ,γ-DIMETHYLALLYL CHLORIDE WITH AMINES, POTASSIUM CYANIDES, AND SALTS OF ORGANIC ACIDS

I. N. Nazarov, V. N. Rakcheev, and L. I. Shmonina

We have shown earlier that compounds that contain a dialkylallyl radical are distinguished by extremely high mobility and tendency to allyl rearrangments. The α,α- and γ,γ-dialkylallylcarbinols are reversibly isomerizable into one another by dilute solutions of sulfuric acid even at room temperature, [1]:

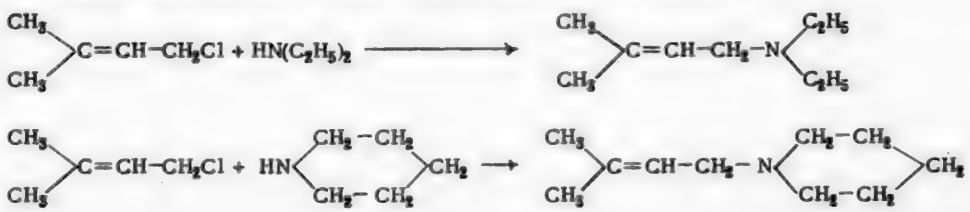


The rearrangement of the dialkylallyl group takes place most readily in some exchange reactions. When dialkylvinyl carbinols are reacted with hydrogen chloride, for example, the principal reaction products are primary α,α-dialkylallyl chlorides, while hydrolysis of the latter causes reversible rearrangement, the dialkylvinylcarbinols being formed again [2]:

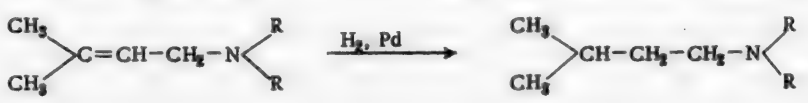


The exchange reactions of dialkylallyl chlorides with potassium acetate are likewise accompanied by rearrangements [2]. But when γ,γ-dialkylallyl chlorides are reacted with alcoholates, the reaction is normal, without any rearrangement, the corresponding primary esters being formed [2]. Nor is rearrangement observed to occur when Grignard reagents (phenylmagnesium bromide) act upon γ,γ-dimethylallyl bromide [3].

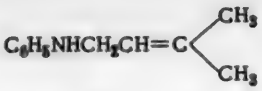
In the light of these facts, it was found desirable to investigate the exchange reactions of γ,γ-dialkylallyl chlorides with amines, salts of organic acids, and potassium cyanide to determine the influence of the nature of the reagents upon the allyl rearrangements. We found that when γ,γ-dimethylallyl chloride is reacted with diethylamine and piperidine, the exchange reaction is normal, without any isomerization, a high yield of the respective tertiary amines, containing the γ,γ-dimethylallyl radical being produced:



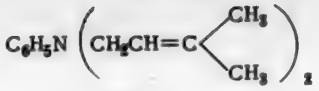
We were unable to find any isomeric tertiary amines, containing a α,α-dimethylallyl radical, in the reaction products. The structure of the synthesized amines was established by hydrogenating them over a Pd catalyst, one molecule of hydrogen being absorbed, which converted them into the known isoamylamines:



γ,γ- Dimethylallyl chloride behaves similarly when reacted with aniline. A mixture of secondary and tertiary amines (I and II) is produced, which is extremely hard to separate:



(I)

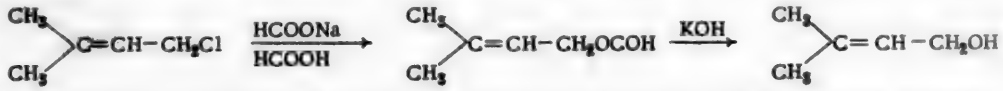


(II)

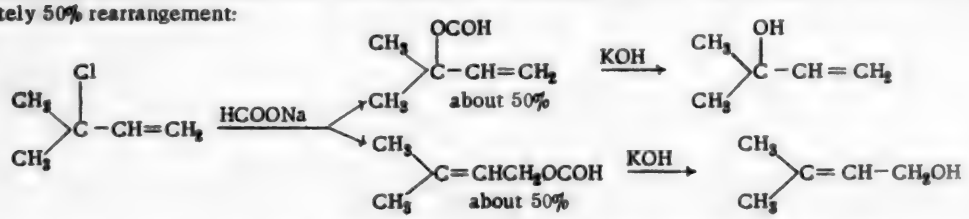
Reacting γ,γ-dimethylallyl chloride with a saturated aqueous solution of potassium cyanide, we again secured a low yield of nothing but the normal reaction product – γ,γ-dimethylallyl cyanide:

This reaction is largely obscured, however, by side processes, chiefly hydrolysis of the chloride.

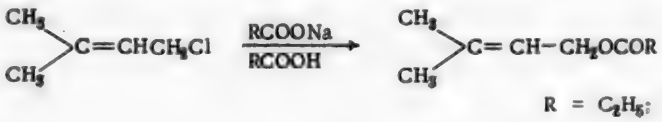
It is worthy of note that the reaction involves no rearrangement when the γ,γ-dimethylallyl chloride is reacted with sodium formate, either, a high yield of the formate of a primary γ,γ-dimethylallyl alcohol being produced, saponification of which with an aqueous alkali yields the γ,γ-dimethylallyl alcohol itself:



As we have shown previously[2], the analogous reaction of γ,γ-dimethylallyl chloride with potassium acetate is accompanied by approximately 30% rearrangement. The reaction of sodium formate with the tertiary α,α-dimethylallyl chloride, however, yields a mixture of nearly equal proportions of the tertiary and primary formates, so that here, as in the reaction with potassium acetate [2], the process involves an approximately 50% rearrangement:



It is much harder to carry out an exchange reaction of γ,γ-dimethylallyl chloride with salts of the higher organic acids than with acetates, or, especially, formates; the only one we have been able to isolate in the pure state is the propionate of γ,γ-dimethyl allyl alcohol. Nor are these reactions accompanied by practically any rearrangements, the principal products being esters of the primary γ,γ-dimethylallyl alcohol:



EXPERIMENTAL

The γ,γ-dimethylallyl chloride used for the exchange reactions was produced, as described previously [2], by reacting gaseous hydrogen chloride with dimethylvinylcarbinol, prepared by the partial hydrogenation of dimethylacetenylcarbinol [4].

Reaction of γ,γ-dimethylallyl chloride with diethylamine. 59 g of freshly distilled diethylamine (b.p. 56-57°) was placed in a three-necked, round-bottomed flask, fitted with a thermometer, a dropping funnel, and a mechanical stirrer, and 42 g of γ,γ-dimethylallyl chloride (b.p. 58-60° at 150 mm; n_D^{20} 1.4475) was added drop by drop with constant stirring. After 40 minutes of stirring, the reaction was so violent that the temperature of the reaction mixture rose to 75°, and the flask had to be cooled with cold water. Stirring was continued for 6 hours at 20°, after which the product was allowed to stand overnight and was stirred the next day for 3 hours at 70-75°. The precipitated diethylamine hydrochloride (20 g) was filtered out and washed with ether, the product being fractionated at a low vacuum at first, and then at atmospheric pressure. This yielded 35 g of diethyl-γ,γ-dimethylallylamine as a colorless liquid with the strong specific odor of a base and a b.p. of 158-160°.

n_D^{20} 1.4390; d_4^{20} 0.7911; MR_D found 47.0; calculated 47.2.

5.749 mg substance: 0.482 ml N_2 (25°, 745 mm). 3.855 mg substance: 0.325 ml N_2 (25°, 745 mm). Found %: N 9.41, 9.47. $C_9H_{19}N$. Calculated %: N 9.90.

The picrate of this amine was readily formed by reacting it with an alcoholic solution of picric acid; it had a m.p. of 101-102° after recrystallization from alcohol. When 10 g of the amine, dissolved in methanol, was hydrogenated with a Pd catalyst, 1800 ml of hydrogen (18°, 746 mm) was absorbed instead of the 1760 ml called for theoretically. Fractionation of the hydrogenation product yielded 7 g of the dimethylisoamylamine described in the literature [5], with a b.p. of 152-153°; n_D^{20} 1.4180. The m.p. of the picrate of this amine was 74-75° (from alcohol), in agreement with the figure given in the literature [5].

Reaction of γ,γ-dimethylallyl chloride with piperidine. We took 25 g of freshly distilled piperidine (b.p. 102-104°) and added 15 g of γ,γ-dimethylallyl chloride a drop at a time. The mixture was stirred for 8 hours at room temperature, set aside to stand overnight, and then again stirred for 8 hours at 65-70° the next day. The precipitated piperidine hydrochloride was filtered out and washed with ether, the product being fractionated, in vacuo at first and then at standard pressure. This yielded 15.3 g of γ,γ-dimethylallylpiperidine, with a b.p. of 79-80° at 14 mm and 193-194° at atmospheric pressure.

n_D^{20} 1.4700; d_4^{20} 0.8586; MR_D found 49.82; calculated 49.65.

5.820 mg substance: 0.469 ml N_2 (23°, 745 mm). 6.610 mg substance: 0.542 ml N_2 (22°, 737 mm). Found %: N 9.11, 9.20. $C_{10}H_{19}N$. Calculated %: N 9.15.

The picrate of γ,γ-dimethylallylpiperidine fused at 145-146° (from alcohol). When 6 g of γ,γ-dimethylallylpiperidine was hydrogenated in an ethyl alcohol solution over a Pd catalyst, 980 ml of hydrogen (21°, 753 mm) was absorbed, instead of the 978 ml called for theoretically. Fractionation yielded 5 g of isoamylpiperidine, with a b.p. of 72-73° at 14 mm.

n_D^{20} 1.4460; d_4^{20} 0.8249; MR_D found 50.28; calculated 50.02.

6.105 mg substance: 0.491 ml N_2 (22°, 740 mm). 6.125 mg substance: 0.496 ml N_2 (22°, 744 mm). Found %: N 9.06, 9.17. $C_{10}H_{21}N$. Calculated %: N 9.03.

The picrate of isoamylpiperidine fuses at 136-137° (from alcohol) and exhibits no depression of the mixed melting point with a synthetic sample.

Reaction of γ,γ-dimethylallyl chloride with aniline. We took 27 g of freshly distilled aniline (b.p. 179.5°) and added 15 g of the chloride, dissolved in 30 ml of anhydrous ether, a drop at a time. The mixture was stirred for 6 hours at room temperature, let stand overnight, and then stirred again for 3 hours at 50° and for 6 hours at 60-65°. The aniline hydrochloride was filtered out, the precipitate washed with ether, and the product fractionated in vacuo. This yielded the following fractions (at 14 mm): I-b.p. 130-135°, 8 g; n_D^{20} 1.5548; II-b.p. 135-170°, 4 g; n_D^{20} 1.5463.

Fraction I consisted chiefly of γ,γ-dimethylallylaniline (I), hydrogenation of which yielded the known isoamylaniline, with a b.p. of 126-130° at 16 mm and n_D^{20} 1.5305 [6]. Fraction II was a mixture of the secondary and tertiary amines (I and II). When it was hydrogenated, it yielded 1.5 g of the diisoamylaniline described in the literature, with a b.p. of 147-150° at 16 mm and n_D^{20} 1.5230 [7].

Action of potassium cyanide upon γ,γ-dimethylallyl chloride. 20 grams of the chloride was added to a solution of 26 g of potassium cyanide in 40 ml of water. The mixture was stirred vigorously for 5 hours at room temperature. The product was extracted with ether, dried with magnesium sulfate, and fractionated, at a low vacuum to begin with and then at atmospheric pressure. This yielded 2 g of the γ,γ-dimethylallyl cyanide described in the literature [8], a liquid with a very sharp nitrile odor, and a b.p. of 97-99° at 112 mm and 162-165° at atmospheric pressure.

n_D^{20} 1.4360; d_4^{20} 0.8572; MR_D found 29.02, calculated 29.21.

Found %: N 14.85, 14.80. C_6H_9N. Calculated %: N 14.74.

In addition to the nitrile, we secured about 2 g of dimethylvinylcarbinol in this experiment, formed as the result of the hydrolysis of the γ,γ-dimethylallyl chloride.

Reaction of sodium formate with γ,γ-dimethylallyl chloride. 41 grams of sodium formate was dissolved in 120 ml of anhydrous formic acid, and 52 g of γ,γ-dimethylallyl chloride (b.p. 56-57° at 140 mm; n_D^{20} 1.4460)

was added to the chilled solution with constant stirring. The mixture was stirred for 2 hours at room temperature (25°). The liquid, which layered at first, became wholly homogeneous later, a heavy precipitate of sodium chloride settling out (29 g). The product was filtered, diluted with water, extracted with ether, washed with a bicarbonate solution, dried with sodium sulfate, and fractionated, at a low vacuum (50 mm) to begin with and then at standard pressure. This yielded 26 g of the formate of γ,γ-dimethylallyl alcohol, a colorless, mobile liquid with a sweetish odor of chloroform and a b.p. of 59-60° at 50 mm and of 131-132° at 700 mm.

n_D^{20} 1.4320; d_4^{20} 0.9329. MR_D found 31.70; calculated 31.10.

8.220 mg substance: 18.91 mg CO_2; 6.68 mg H_2O. 4.965 mg substance: 11.43 mg CO_2; 4.26 mg H_2O. Found %: C 63.0, 62.8; H 9.1, 9.2 $C_6H_{10}O_2$. Calculated %: C 63.1; H 8.8.

When the sodium formate is reacted with the γ,γ-dimethylallyl chloride while heated (55-60°), much of the product becomes tarred.

Saponifying the formate of γ,γ-dimethylallyl alcohol.

a) 6 g of the formate described above was mixed with a solution of 3.5 g of potassium hydroxide in 50 ml of water, and the mixture was stirred vigorously for 6 hours at room temperature and then for 12 hours at 50°. After the aqueous layer had been saturated with potash, the product was extracted with ether, dried with potash, and fractionated. This yielded 4 g of γ,γ-dimethylallyl alcohol, with a b.p. of 138-139° at 700 mm; n_D^{20} 1.4420.

b) 52 grams of γ,γ-dimethylallyl chloride was added to 41 g of sodium formate dissolved in 120 ml of anhydrous formic acid, and the mixture was stirred at room temperature for 2 hours. The precipitated sodium chloride (29 g) was filtered out, and the product diluted with water (300 ml), extracted with ether, washed with a bicarbonate solution, and dried with sodium sulfate. The formate of γ,γ-dimethylallyl alcohol secured after the ether had been driven off was saponified without being distilled, as described above, using a 10% solution of potassium hydroxide (300 ml). Thorough fractionation of the hydrolysis products into a column yielded 1,2 g of α,α-dimethylallyl alcohol (b.p. 90-94° at 710 mm; n_D^{20} 1.4125) and 26 g of γ,γ-dimethylallyl alcohol (b.p. 139-140° at 710 mm; n_D^{20} 1.4410).

The α,α-dimethylallyl alcohol was most likely produced in this experiment by the hydrolysis of the unreacted γ,γ-dimethylallyl chloride.

Action of sodium formate on α,α-dimethylallyl chloride. 23.5 grams of α,α-dimethylallyl chloride (b.p. 36-38° at 140 mm; n_D^{20} 1.4180), was added to a solution of 18 g of sodium formate in 60 ml of anhydrous formic acid, and the mixture was stirred for 3 hours at room temperature (20°). The product was processed like the preceding one, the resultant formate being saponified with a 10% solution of potassium hydroxide (150 ml) as described above, without distillation. Thorough fractionation of the saponification products yielded 4.5 g of dimethylvinylcarbinol (b.p. 93-96° at 710 mm; n_D^{20} 1.4130) and 5 g of γ,γ-dimethylallyl alcohol (b.p. 138-140° at 710 mm; n_D^{20} 1.4420).

Reaction of sodium propionate with γ,γ-dimethylallyl chloride. 25 grams of sodium propionate was dissolved in 75 ml of propionic acid (b.p. 138-141°), and to the solution was added 26 g of its chloride (b.p. 57-60° at 150 mm; n_D^{20} 1.4460). The homogeneous mixture was stirred for 2 hours at room temperature (20°), 12 hours at 50-60°, and 10 hours at 70-80°. The 14.4 g of precipitated sodium chloride was filtered out, and the product diluted with water, extracted with ether, washed with a bicarbonate solution, and fractionated, in vacuo at first and then at atmospheric pressure. This yielded 11 g of the propionate of γ,γ-dimethylallyl alcohol as a colorless, mobile, fragrant liquid with a b.p. of 162-164° at 710 mm.

n_D^{20} 1.4310; d_4^{20} 0.9111; MR_D found 40.35; calculated 40.34.

4.46 mg substance: 11.02 mg CO_2; 4.25 mg H_2O. 4.91 mg substance: 12.13 mg CO_2; 4.61 mg H_2O. Found %: C 67.4, 67.3; H 10.3, 10.2. $C_8H_{14}O_2$. Calculated %: C 67.6; H 9.9.

Saponifying the propionate of γ,γ-dimethylallyl alcohol. 4 grams of the propionate described above was stirred vigorously with 30 ml of 10% aqueous potassium hydroxide for 3 hours at room temperature and 16 hours at 50°. The product was extracted with ether, dried with potash, and fractionated. This yielded 2.2 g of γ,γ-dimethylallyl alcohol, with a b.p. of 137-139° at 700 mm and n_D^{20} 1.4410.

Reaction of γ,γ-dimethylallyl chloride with sodium butyrate. 60 grams of sodium butyrate was dissolved in 150 ml of butyric acid, 52 g of γ,γ-dimethylallyl chloride was added, and the mixture was stirred for 10 hours at 70-80°. The precipitated sodium chloride (24 g) was filtered out, and the solution

was reheated to 70-80° for 16 hours. The precipitated 3.5 g of sodium chloride was filtered out, and the solution was reheated for another 8 hours at 70-80°, but no more sodium chloride was precipitated. The product was diluted with water (300 ml), extracted with ether, washed with a soda solution, and dried with sodium sulfate. The butyrate of γ,γ-dimethylallyl alcohol secured after the ether had been driven off was saponified with an aqueous alkali (200 ml of 10% sodium hydroxide, 6 hours of heating to 80°). Extraction of the saponification products with ether, drying, and careful fractionation yielded 6 g of dimethylvinylcarbinol (b.p. 92-95° at 700 mm; n_D^{20} 1.4120) and 20 g of γ,γ-dimethylallyl alcohol (b.p. 137-139° at 700 mm; n_D^{20} 1.4410).

SUMMARY

The reaction of γ,γ-dimethylallyl chloride with diethylamine and piperidine yields about 70% of the respective tertiary amines, containing a γ,γ-dimethylallyl radical. These exchange reactions are normal, not involving allyl rearrangements. γ,γ-dimethylallyl chloride reacts similarly with potassium cyanide, producing a yield of some 10% of γ,γ-dimethylallyl cyanide, and with sodium formate, producing about 50% of the formate of γ,γ-dimethylallyl alcohol.

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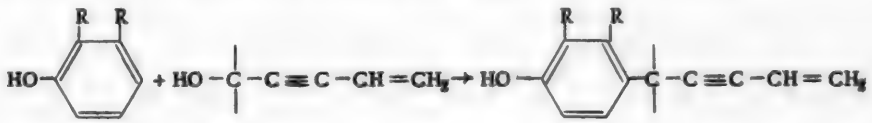
136. CONDENSATION OF 5-METHYL-1,3-HEXADIEN-5-OL AND 5-METHYLHEXAN-5-OL WITH PHENOL IN THE PRESENCE OF PHOSPHORIC ACID

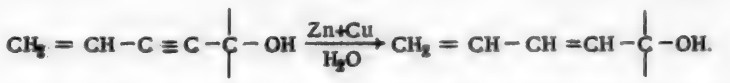
I. N. Nazarov and A. I. Kakhniashvili

In our laboratory we previously condensed phenols with vinylacetylenic alcohols, thus synthesizing for the first time substitution derivatives of phenol with a vinylacetylenic structure [1]:

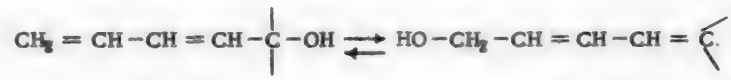


R = H or CH_3

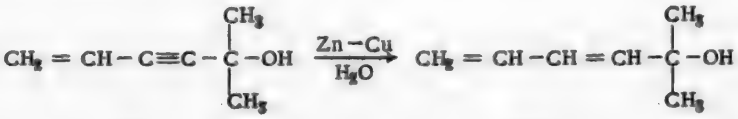
We were also interested in investigating the condensation of phenols with 1,3-diene alcohols, which are produced by the selective hydrogenation of vinylacetylenic alcohols with coppered zinc dust and water [2]:



No work at all has been done up to the present time on the condensation of 1,3-diene alcohols with aromatic compounds and with phenols in particular. These condensations are likewise of interest because the 1,3-diene alcohols readily undergo diene rearrangements when acted upon by acids, the hydroxyl group being shifted to the delta position and two double bonds being displaced, as has been demonstrated on numerous occasions in our laboratory [3]:

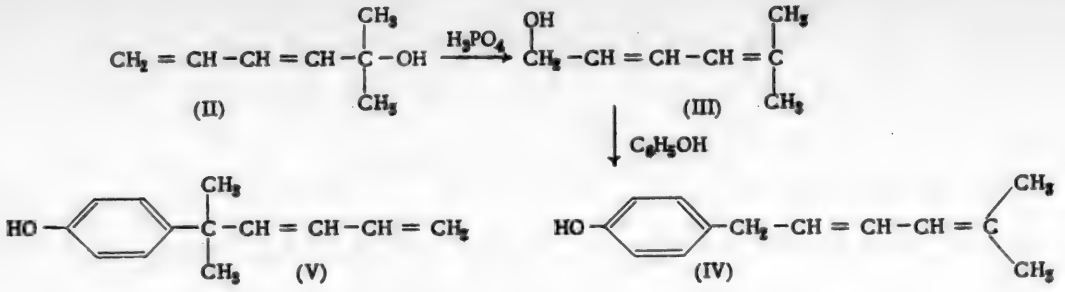


We were interested in determining how these diene rearrangements would affect the condensation of 1,3-diene alcohols with phenols when acids were present. To test these condensations we chose, first of all, the most readily available 5-methyl-1,3-hexadien-5-ol (II), prepared by the selective hydrogenation of dimethylvinylethynylcarbinol (I) [2]:

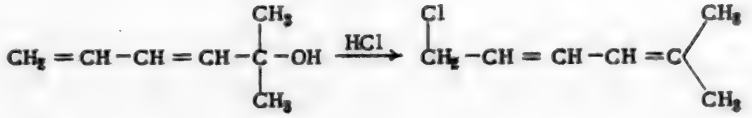


(I) (II)

When phosphoric acid is present, the diene carbinol (II) condenses with phenol much more vigorously than does the vinylacetylenic alcohol (I), resulting in the formation of a para-substituted diene phenol (IV), which corresponds to the isomeric primary diene carbinol (III) rather than to the original tertiary diene alcohol (II):

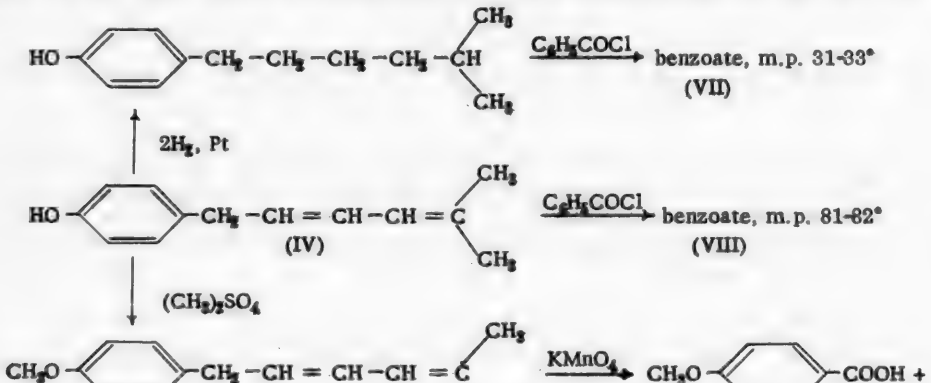


Hence, the condensation of phenol with the tertiary diene alcohol (III) involves a diene isomerization, such as occurs when this carbinol is acted upon by hydrogen chloride [4]:

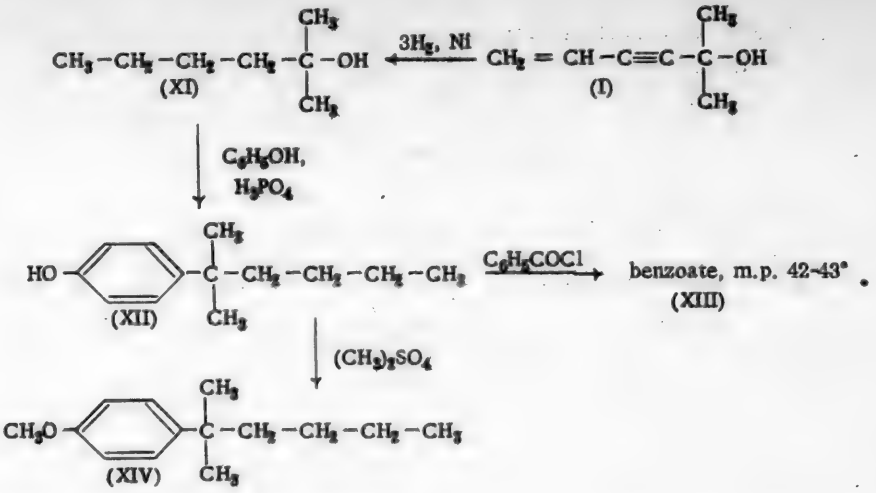


We were unable to detect the tertiary diene phenol (V) that corresponds to the tertiary diene phenol (II) in the condensation products of the latter with phenol. When the diene phenol (IV) was hydrogenated with a Pd catalyst, the two molecules of hydrogen called for theoretically were absorbed, the phenol being converted into p-isoheptylphenol (VI).

Methylation of the diene phenol (IV) with dimethyl sulfate yielded its methyl ether (IX), oxidation of which with permanganate yielded anisic acid (X), oxalic acid, and acetone. Benzoylation of the phenols (IV) and (VI) with benzoyl chloride yielded the corresponding crystalline benzoates (VII) and (VIII).



By way of comparison, we also condensed phenol with dimethylbutylcarbinol (XI), prepared by exhaustively hydrogenating dimethylvinylethynylcarbinol (I) with Raney's nickel. This condensation yielded the dimethylbutyl-p-hydroxyphenylmethane (XII), previously described in the literature [5], which was converted into the corresponding crystalline benzoate (XII) and methyl ether (XIV).



EXPERIMENTAL

5-Methyl-1,3-hexadien-5-ol was prepared by hydrogenating dimethylvinylethynylcarbinol with coppered zinc dust and water, as described previously [2]. The traces of the original dimethylvinylethynylcarbinol were eliminated from the hydrogenated product by heating the latter with 1% powdered potassium hydroxide at 110-130° until no more vinylacetylene was evolved.

Condensation of 5-methyl-1,3-hexadien-5-ol with phenol in the presence of phosphoric acid. 11 grams of 5-methyl-1,3-hexadien-5-ol (b.p. 45-47° at 12 mm; n_D^{20} 1.4720) was added drop by drop, with constant stirring, at room temperature to a mixture of 9 g of phenol and 10 ml of phosphoric acid (sp. gr. 1.693). The reaction was accompanied by the evolution of heat, the temperature rising to 44° by the time all the carbinol had been added. Stirring was continued for another 3 hours after the carbinol had been added. The reaction mass was diluted with ether, washed with water, and then washed several times with a 10% solution of sodium hydroxide to extract the acid reaction products.

The alkaline extracts were combined, acidulated with dilute hydrochloric acid, and extracted with ether, the ether solution being dried with magnesium sulfate, the ether driven off, and the remaining acid products distilled in vacuo. This yielded 2.7 g of the unreacted phenol (b.p. 55-68° at 3 mm) and 5.5 g of a diene phenol (IV) with a b.p. of 122-127° at 2.5 mm. The polymer residue totaled 4 g. The ether solution, which contained neutral products, was fractionated, yielding 1.6 g of a substance with a b.p. of 95-135°; n_D^{20} 1.536. The polymer residue totaled 1.8 g.

The diene phenol (IV) distilled without decomposition at 122-124° and 2.5 mm, solidified into a hard crystalline mass, and fused at 48.5-50°. It was soluble in alkalies, alcohol, ether, acetone, and benzene. It underwent no change in storage.

3.725 mg substance: 11.290 mg CO_2; 2.870 mg H_2O. 5.805 mg substance; 17.595 mg CO_2; 4.475 mg H_2O. Found %: C 82.71, 82.72; H 8.62, 8.62. $C_{13}H_{16}O$. Calculated %: C 82.97; H 8.51.

Condensation of the diene phenol (IV) with benzoyl chloride. 1 gram of the diene phenol (IV) was dissolved in 10 ml of 10% sodium hydroxide, and 2 g of benzoyl chloride was added gradually. An oily substance settled out, which crystallized the next day; the crystals were filtered out and recrystallized from alcohol. This yielded 0.55 g of a benzoyl derivative of the diene phenol (VIII) as white crystals with a m.p. of 81-82.5°.

8.83 mg substance: 26.39 mg CO_2; 5.49 mg H_2O. 10.56 mg substance: 31.65 mg CO_2; 6.94 mg H_2O. Found %: C 81.56, 81.79; H 6.96, 6.94. $C_{20}H_{20}O_2$. Calculated %: C 82.19; H 6.84.

Methylating the diene phenol (IV) with dimethyl sulfate. 7 grams of the diene phenol (IV) was dissolved in 50 ml of 10% sodium hydroxide, and 12 ml of dimethyl sulfate was gradually added. The mixture was agitated for half an hour; heat was evolved during the reaction.. Then a solution of sodium hydroxide was added until the reaction was alkaline, and the liquid was heated to the boiling point. After the liquid had cooled, the product was extracted with ether, dried with potash, and distilled in vacuo. This yielded 2.5 g

of the methyl ether of the dien phenol (IX) as a colorless, transparent liquid with a b.p. of 153-156° at 5 mm.

n_D^{19} 1.5490; d_4^{19} 0.9582; MR_D found 64.04; calculated 63.84.

10.70 mg substance: 32.52 mg CO_2; 9.02 mg H_2O. 15.74 mg substance: 47.96 mg CO_2; 13.09 mg H_2O
Found %: C 82.94, 83.14; H 9.43, 9.25. $C_{14}H_{18}O$. Calculated %: C 83.16, H 8.91.

Hydrogenating the diene phenol (IV). When 3 g of the substance, dissolved in 50 ml of diethyl ether, was hydrogenated with a platinum catalyst prepared by the Adams method, 775 ml of hydrogen was absorbed (the theory calling for 784 ml of hydrogen). The catalyst was filtered out, the alcohol driven off, and the product distilled in vacuo. This yielded 2.4 g of p-isoheptylphenol (VI), with a b.p. of 282-283° at 746 mm; n_D^{20} 1.505.

5.035 mg substance: 14.920 mg CO_2; 4.765 mg H_2O. 4.560 mg substance: 13.525 mg CO_2; 4.310 mg H_2O.
Found %: C 81.04, 80.94; H 10.61, 10.58. $C_{13}H_{20}O$. Calculated %: C 81.25; H 10.42.

Condensing p-isoheptylphenol (VI) with benzoyl chloride. 1 gram of p-isoheptylphenol (VI) was dissolved in 10 ml of 10% sodium hydroxide, and 2 g of benzoyl chloride was added gradually. An oily substance settled out, which crystallized when the mixture was chilled with a freezing mixture (ice + salt). The filtered-out crystals were recrystallized from alcohol, yielding 0.5 g of the benzoyl derivative of p-isoheptylphenol (VII), with a m.p. of 31-33°.

5.190 mg substance: 15.439 mg CO_2; 3.936 mg H_2O. 6.695 mg substance: 19.919 mg CO_2; 5.140 mg H_2O.
Found %: C 81.18, 81.20; H 8.50, 8.58. $C_{20}H_{24}O_2$. Calculated %: C 81.03; H 8.16.

Oxidizing the methyl ether of the diene phenol (IX) with permanganate. 1.7 g of the substance was placed in a solution of 0.4 g of potash in 100 ml of water. Then 6.8 g of pulverized potassium permanganate was gradually added to the resulting mixture, with vigorous stirring and cooling with ice water (the temperature of the mixture did not rise above 1°). Oxidation lasted 12 hours. The manganese dioxide was filtered out and washed several times with hot water. 160 ml of water was driven off together with the volatile neutral products from the 250 ml of the combined filtrate. The distillate displayed a positive iodoform reaction. The distillate was saturated with potash while chilled with ice water, and another 60 ml of liquid was driven off from it. The distillate was resaturated with potash, and another 20 ml of liquid was driven off and saturated with potash, after which 6 ml more of a liquid with the obvious odor of acetone was driven off from the latter. The 2,4-dinitrophenylhydrazone prepared from this distillate had a m.p. of 124-126° after recrystallization from ethyl alcohol. Its mixed melting point with the known 2,4-dinitrophenylhydrazone of acetone exhibited no depression.

The residue left after the neutral products had been driven off was acidulated with hydrochloric acid. The crystals were filtered out, washed several times with water, and dried in a desiccator. This yielded 0.55 g of p-methoxybenzoic acid, which had a m.p. of 179-181° after recrystallization from water. Its mixed melting point with known p-methoxybenzoic acid exhibited no depression. After the crystals of p-methoxybenzoic acid had been filtered out, the filtrate was neutralized with ammonia and heated to a boil, a hot solution of calcium chloride being added to this solution while hot. Crystals of calcium oxalate, which decolorized permanganate, settled out.

Condensing dimethylbutylcarbinol with phenol in the presence of phosphoric acid. 70 grams of dimethylbutylcarbinol (b.p. 140-142°) was added drop by drop with constant stirring at a temperature of 65° to a mixture of 54 g of phenol and 27 ml of phosphoric acid (sp. gr. 1.82). The mixture was stirred for 17 hours at 80-90°. After it had cooled, the product was extracted with ether, and the ether solution was washed with water and then repeatedly with a 10% solution of sodium hydroxide to extract the acid reaction products.

The alkaline solutions were combined and acidulated with dilute hydrochloric acid and the product was extracted with ether. The ether solution was dried with potash, the ether was driven off, and the remaining acid products were distilled at atmospheric pressure. This yielded the following fractions: I — b.p. 178-180°, 28 g (phenol); II — b.p. 268-272°, 13 g; n_D^{20} 1.5149; tarry residue — 2 g. Redistillation of Fraction II yielded 10.5 g of the dimethylbutyl-p-hydroxyphenylmethane (XII) described previously, as a slightly yellowish liquid with the odor of phenol, b.p. 270-272°.

n_D^{20} 1.5155; d_4^{20} 0.9522; MR_D found 59.83; calculated 60.085.

3.861 mg substance: 14.425 mg CO_2; 3.615 mg H_2O. 3.785 mg substance: 11.205 mg CO_2; 3.575 mg H_2O.
Found %: C 80.75, 80.79; H 10.68, 10.56. $C_{13}H_{20}O$. Calculated %: C 81.25; H 10.42.

The ether solution containing the neutral products yielded 16 g of 2-methyl-2-hexene (b.p. 93-95°; n_D^{19} 1.413), produced by the dehydration of the dimethylbutylcarbinol. The neutral products also yielded 16 g of a mixture of high-boiling products (b.p. 70-148°; n_D^{19} 1.505), which was not investigated further.

Methylating dimethylbutyl-p-hydroxyphenylmethane (XII) with dimethyl sulfate. 5 grams of the substituted

phenol (XII) was dissolved in 25 ml of 10% sodium hydroxide, and 8 ml of dimethyl sulfate was added gradually. The mixture was agitated for half an hour (heat was evolved during the reaction), and then a solution of sodium hydroxide was added until the reaction was alkaline, and the liquid was heated to a boil. After it had cooled, the product was extracted with ether, dried with potash, and fractionated in vacuo. This yielded 2.5 g of the methyl ether (XIV) with a b.p. of 104-105° at 3 mm.

n_D^{20} 1.5020; d_4^{20} 0.9349; MR_D found 64.97; calculated 64.78.

3.045 mg substance: 9.054 mg CO_2; 2.960 mg H_2O. 7.214 mg substance: 21.489 mg CO_2; 6.915 mg H_2O. Found %: C 81.14, 81.30; H 10.85, 10.70. $C_{14}H_{22}O$. Calculated %: C 81.55; H 10.67.

Condensing dimethylbutyl-p-hydroxyphenylmethane (XII) with benzoyl chloride. 1 g of the substituted phenol (XII) was dissolved in 10 ml of 10% sodium hydroxide, and 2 g of benzoyl chloride was slowly added. An oil settled out, which crystallized the next day. The crystals were filtered out and recrystallized from alcohol. This yielded 0.7 g of the benzoyl derivative (XIII) described previously, with a m.p. of 42-43°.

11.45 mg substance: 34.01 mg CO_2; 8.51 mg H_2O. 11.33 mg substance: 33.79 mg CO_2; 8.39 mg H_2O. Found %: C 81.06, 81.30; H 8.35, 8.24. $C_{20}H_{24}O_2$. Calculated %: C 81.03; H 8.16.

SUMMARY

The condensation of 5-methyl-1,3-hexadien-5-ol (II) with phenol in the presence of phosphoric acid involves a rearrangement, in which a para-substituted diene phenol (IV) is produced, corresponding to the primary diene alcohol (III).

Methylating the diene phenol (IV) with dimethyl sulfate yields a methyl ether (IX), oxidation of which with permanganate yields anisic acid, oxalic acid, and acetone. Two molecules of hydrogen are absorbed when the diene phenol (IV) is hydrogenated catalytically, p-isoheptylphenol (VI) being produced.

It is much harder to condense 5-methylhexan-5-ol (XI) with phenol in the presence of phosphoric acid, the normal condensation product — the tertiary para-substituted phenol (XII) — being formed. Benzoylating the phenols (IV, VI, and XII) with benzoyl chloride yielded the respective crystalline benzoates.

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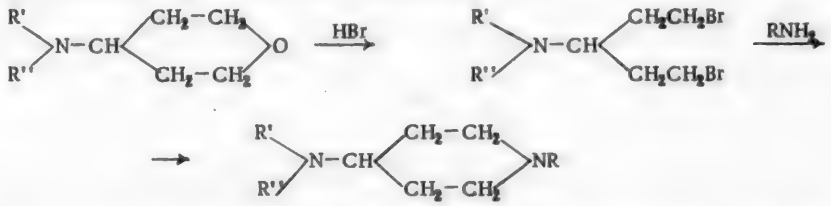
DERIVATIVES OF ACETYLENE

137. HETEROCYCLIC COMPOUNDS

XIII. THE REACTION OF 4-PIPERIDONES WITH PRIMARY AMINES. SYNTHESIS OF 4-IMINO- AND 4-AMINOPIPERIDINES

I.N. Nazarov and V.A. Rudenko

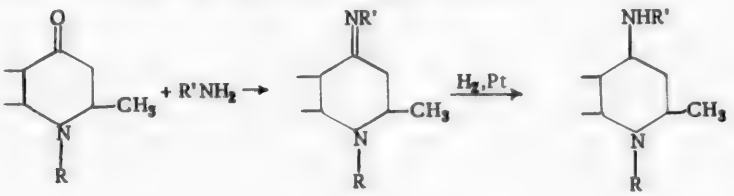
Among the numerous papers on the synthesis and investigation of amines that possess spasmolytic action the researches on the substitution derivatives of 4-aminopiperidines occupy an important place. Most of the compounds of this group, which mainly contain a tertiary amino group, were synthesized by Hahn, Cerkovnikov, and Prelog [1] by reacting the primary amines with 1,5-dibromo-3-aminopentanes, which were produced in turn by reacting fuming hydrobromic acid with the respective 4-aminotetrahydropyrans:



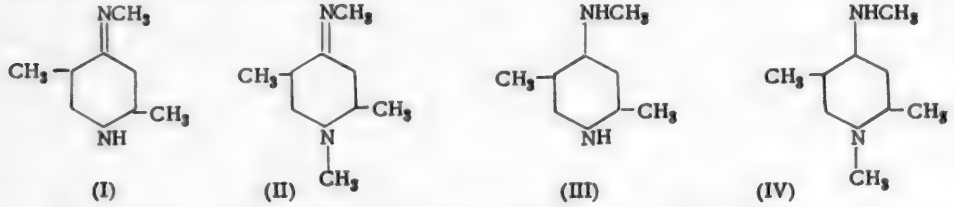
Some of the synthesized compounds of this series exhibit greater spasmolytic action than papaverine. But the complexities of the synthesis, particularly of the members containing an amino group, greatly limit the possibilities of investigating this interesting series of amines.

In our preceding paper [2], which described a new method of synthesizing the substituted δ-piperidones by reacting vinyl allyl ketones with ammonia and primary amines, we noted that in several instances the analysis of the synthesized δ-piperidones indicated an excessively high percentage of nitrogen, whereas analysis of the picrates of these piperidones yielded the theoretical results. This circumstance compelled us to assume that the excessively high percentage of nitrogen in some of the δ-piperidones, synthesized by the action of an excess of methylamine on the vinyl allyl ketones, is due to traces of 4-methylaminopiperidines, products of the reaction of the δ-piperidones with monomethylamine.

The present research had as its objectives proving that 4-methyliminopiperidines were present in the products of the reaction between substitution derivatives of vinyl allyl ketone and monomethylamine (when the latter is present in considerable excess) and synthesizing 4-iminopiperidines by reacting various primary amines with the δ-piperidones, which would make it possible to effect the transition to the 4-aminopiperidines, i.e. to a series of substances that exhibit spasmolytic activity. We found that when the δ-piperidones were heated on a water bath with primary amines (methylamine, ethylamine, and aniline), the readily hydrolyzable 4-iminopiperidines were actually produced, their hydrogenation yielding the respective 4-aminopiperidines:

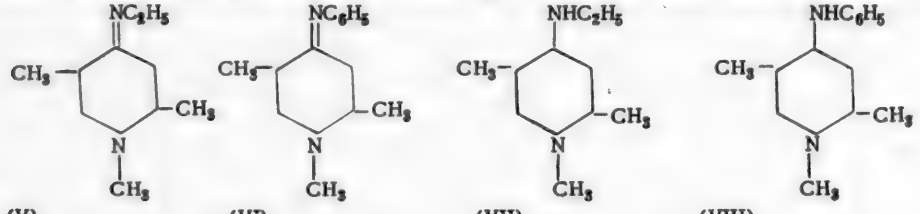


When monomethylamine is heated in a metallic ampoule with 2,5-dimethyl-4-piperidone or 1,2,5-trimethyl-4-piperidone, we get 2,5-dimethyl-4-methyliminopiperidine (I) and 1,2,5-trimethyl-4-methyliminopiperidine (II), respectively, neither of which could be easily isolated in the pure state. But the respective hydrogenated products — 2,5-dimethyl-4-methylaminopiperidine (III) and 1,2,5-trimethyl-4-methylaminopiperidine (IV) — could be readily recovered in the pure state by hydrogenating the major fractions over a Pt catalyst in both instances:

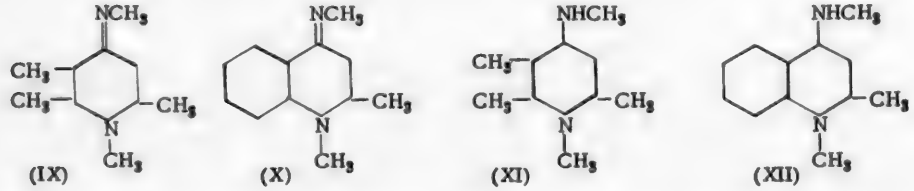


When 1,2,5-trimethyl-4-piperidone was heated with ethylamine and aniline, distillation in vacuo readily yielded 1,2,5-trimethyl-4-ethyliminopiperidine (V) and 1,2,5-trimethyl-4-phenyliminopiperidine (VI) in the pure state.

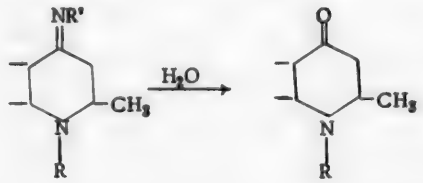
Hydrogenating 1,2,5-trimethyl-4-ethyliminopiperidine (V) in alcohol over a Pt catalyst converted it into 1,2,5-trimethyl-4-ethylaminopiperidine (VII). 1,2,5-Trimethyl-4-phenyliminopiperidine (VI) is hydrogenated over a Pt catalyst very slowly; adding palladium and nickel catalysts did not speed up hydrogenation. The 1,2,5-trimethyl-4-phenyliminopiperidine was reduced by reacting an alcoholic solution of the imino compound with metallic sodium. Distillation of the reduction product in vacuo yielded 1,2,5-trimethyl-4-phenylaminopiperidine (VIII):



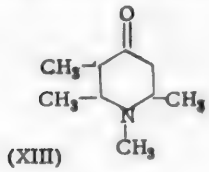
Heating 1,2,3,6-tetramethyl-4-piperidone (XIII) and 1,2-dimethyl-4-ketodecahydroquinoline (XVII) on a water bath with monomethylamine, followed by fractionation of the reaction products in vacuo yielded 1,2,3,6-tetramethyl-4-methyliminopiperidine (IX) and 1,2-dimethyl-4-methyliminodecahydroquinoline (X). The results of our analysis for the percent of nitrogen in the resultant preparations (IX) and (X) proved to be somewhat low, owing to the proximity of the boiling points of the synthesized imino compounds to those of the initial piperidones. Reducing these compounds with hydrogen over a Pt catalyst in alcoholic solution, however, yielded the analytically pure 1,2,3,6-tetramethyl-4-methylaminopiperidine (XI) and 1,2-dimethyl-4-methylaminodecahydroquinoline (XII):

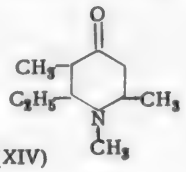


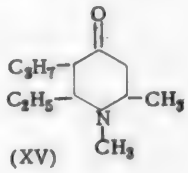
When all the 4-iminopiperidines described in this paper were heated with water or dilute hydrochloric acid, they were completely hydrolyzed into the respective γ-piperidones:

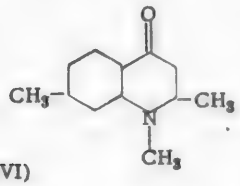


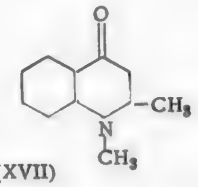
Thus, the 3-piperidones can be readily freed of any traces of the respective 4-iminopiperidines they may contain, as has been shown in the 1,2,3,6-tetramethyl-4-piperidone (XIII), the 1,2,5-trimethyl-6-ethyl-4-piperidone (XIV), the 1,2-dimethyl-6-ethyl-5-propyl-4-piperidone (XV), the 1,2,7-trimethyl-4-ketodecahydroquinoline (XVI), and the 1,2-dimethyl-4-ketodecahydroquinoline (XVII), which were previously synthesized by reacting the corresponding derivatives of vinyl allyl ketone with an excess of methylamine and contained appreciable quantities of 4-imino derivatives as impurities.


(XIII)


(XIV)


(XV)


(XVI)


(XVII)

The 4-iminopiperidines are mobile liquids with the strong unpleasant odors of bases. They quickly turn yellow when allowed to stand, and tar when kept for a long time exposed to the air. The 4-iminopiperidines should be distilled in a current of well-dried nitrogen because of their instability and tendency to hydrolyze.

EXPERIMENTAL

2,5-Dimethyl-4-methylaminopiperidine (III). 26.5 g of 2,5-dimethyl-4-piperidone (b.p. 71-73° at 8 mm; n_D^{19} 1.4650) was saturated with gaseous methylamine, the flask being chilled with an ice-salt mixture, after which 6.6 g of methylamine was added, and the mixture was heated for 6 hours in a metal ampoule to 90-95°. After heating was over, the reaction product was distilled in vacuo in a current of anhydrous nitrogen. After a small head fraction (1.6 g), containing water and the initial piperidone, had been driven off, we secured 21 g of a mixture of the initial piperidone and 2,5-dimethyl-4-iminopiperidine (I), b.p. 78-81° at 10 mm; n_D^{20} 1.4780. In view of the fact that it was impossible to separate this mixture by fractionation in vacuo, it was hydrogenated catalytically with a platinum catalyst in a solution of 40 ml of ethyl alcohol. Only after 6 hours had elapsed did the absorption of hydrogen set in; it continued for 15 hours, 2280 ml of hydrogen being absorbed. The alcohol was driven off, and the hydrogenation product was repeatedly fractionated in vacuo. This yielded 4.5 g of pure 2,5-dimethyl-4-methylaminopiperidine (III) with a b.p. of 67° at 7.5 mm:

n_D^{20} 1.4720; d_4^{20} 0.9043. MR_D found 44.15; calculated 44.05.

3.345 mg substance: 8.260 mg CO_2; 3.780 mg H_2O. 5.195 mg substance: 12.868 mg CO_2; 5.941 mg H_2O. 3.817 mg substance: 0.655 ml N_2 (25°, 743 mm). 4.730 mg substance: 0.792 ml N_2 (24°, 757 mm). Found %: C 67.39, 67.57; H 12.64, 12.80; N 19.22, 19.17. $C_9H_{18}N_2$. Calculated %: C 67.55; H 12.76; N 19.69.

The picrate of 2,5-dimethyl-4-methylaminopiperidine, prepared by mixing the base with an alcoholic solution of picric acid, had a m.p. of 220° (from alcohol).

In addition to the 2,5-dimethyl-4-methylaminopiperidine, this experiment yielded 12 g of a crystalline mixture of the isomeric 2,5-dimethyl-4-hydroxypiperidines (m.p. 68-110°), produced by the catalytic reduction of the carbonyl group in 2,5-dimethyl-4-piperidone.

1,2,5-Trimethyl-4-methyliminopiperidine (II). 13.4 g of 1,2,5-trimethyl-4-piperidone (b.p. 70-72° at 8 mm; n_D^{21} 1.4582), after which 6.6 g methylamine was chilled (ice-salt mixture), saturated with gaseous methylamine (125% excess) was added, and the mixture heated to 70-75° for 4 hours in a metal ampoule on a water bath. After the excess methylamine had been driven off, the faintly colored reaction product was distilled in vacuo in a current of anhydrous nitrogen. Fractionation yielded the following fractions (at 8 mm): Fraction I) 76-78°; n_D^{21} 1.4697 — 9.0 g; Fraction II) 78-80°; n_D^{21} 1.4732 — 3.7 g.

The first fraction was again saturated with gaseous methylamine under the same conditions as before and heated to 75° for 4 hours. The reaction product secured after vacuum fractionation in a current of nitrogen totaled 5.5 g (b.p. 78-80° at 8 mm; n_D^{21} 1.4746); it was combined with Fraction II, and the whole was then redistilled in vacuo (at 8 mm) in a current of anhydrous nitrogen: Fraction I – 76-78°; n_D^{20} 1.4748, 5.3 g; and Fraction II – 78-80°; n_D^{20} 1.4752, 3.8 g.

Fraction II was 1,2,5-trimethyl-4-methyliminopiperidine (II), a colorless liquid that rapidly turned yellow upon standing. B.p. 78-80° at 8 mm.

n_D^{20} 1.4752; d_4^{20} 0.9118. MR_D Found 47.65; calculated 48.18.

7.025 mg substance: 1.045 ml N_2 (22°, 749 mm). 5.990 mg substance: 0.885 ml N_2 (22°, 750 mm). Found %: N 16.96, 16.87. $C_9H_{18}N_2$. Calculated %: N 18.16.

As the analysis showed, the synthesized 1,2,5-trimethyl-4-methyliminopiperidine was not entirely pure, containing a slight trace of 1,2,5-trimethyl-4-piperidone.

When we tried to secure the picrate of 1,2,5-trimethyl-4-methyliminopiperidine by reacting the reaction product with a saturated alcoholic solution of picric acid, all we got was the picrate of 1 2 5-trimethyl-4-piperidone, m.p. 161-162° from alcohol.

4.415 mg substance: 0.583 ml N_2 (23°, 749 mm). 4.640 mg substance: 0.613 ml N_2 (23°, 750 mm). Found %: N 15.01, 15.04. $C_{14}H_{18}O_8N_4$. Calculated %: N 15.135.

Hydrolysis of 1,2,5-trimethyl-4-methyliminopiperidine. 3.5 g of the 1,2,5-trimethyl-4-methyliminopiperidine (b.p. 78-80° at 8 mm; n_D^{20} 1.4752) described above was dissolved in 40 ml of water, and the solution was allowed to stand at room temperature for 20 hours, after which it was heated to 80-90° for 4.5 hours. After having been salted out with potash, the hydrolysis product was extracted with ether, dried with potash, and distilled in vacuo. This yielded 2.3 g of 1,2,5-trimethyl-4-piperidone with a b.p. of 74-75° at 8 mm; n_D^{18} 1.4615. Its picrate had a m.p. of 161° and exhibited no depression when mixed with the picrate of known 1,2,5-trimethyl-4-piperidone.

1,2,5-Trimethyl-4-methylaminopiperidine (IV). 5.3 g of 1,2,5 trimethyl-4-methyliminopiperidine (b.p. 76-78° at 8 mm; n_D^{20} 1.4748) was hydrogenated in 10 ml of absolute alcohol with a platinum catalyst. The absorption of hydrogen set in only after 3.5 hours had elapsed and lasted 40 minutes, 820 ml of hydrogen being absorbed.

After the catalyst had been filtered out and the solvent had been driven off, the hydrogenated product was fractionated in vacuo (at 8 mm): Fraction I) 74-76°; n_D^{18} 1.4592 – 0.9 g; Fraction II) 76-81°; n_D^{18} 1.4652 – 3.3 g.

Double distillation of the latter fraction in vacuo yielded 1.9 g of pure 1,2,5-trimethyl-4-methylaminopiperidine (IV) as a colorless liquid with a strong amine odor, b.p. 72-73° at 7 mm:

n_D^{20} 1.4637; d_4^{20} 0.8828. MR_D found 48.97; calculated 49.10.

3.975 mg substance: 10.030 mg CO_2; 4.530 mg H_2O. 4.280 mg substance: 10.810 mg CO_2; 4.870 mg H_2O. Found %: C 68.86, 68.93; H 12.75, 12.73. $C_9H_{20}N_2$. Calculated %: C 69.17; H 12.90.

Picrate: . m.p. 234-235° (from 50% alcohol).

1,2,5-Trimethyl-4-ethyliminopiperidine (V). 10.6 g of 1,2,5-trimethyl-4-piperidone (b.p. 70-72° at 8 mm; n_D^{21} 1.4582) was mixed with 7.4 g of ethylamine (approximately 120% excess), and the mixture was heated to 65-70° for 3 hours in a steel ampoule. The light-yellow reaction product was dried with potash, the excess ethylamine was driven off, and the residue was vacuum-fractionated in a current of anhydrous nitrogen. This yielded 9 g of 1,2,5-trimethyl-4-ethyliminopiperidine (V) as a mobile, colorless liquid with the strong odor of pyridine bases. M.p. 82-83.5° at 8 mm.

n_D^{20} 1.4690; d_4^{20} 0.8915. MR_D found 52.57; calculated 52.80.

8.195 mg substance: 1.176 ml N_2 (21°, 754 mm). 5.208 mg substance: 0.766 ml N_2 (23°, 739 mm). Found %: N 16.53, 16.49. $C_{10}H_{20}N_2$. Calculated %: N 16.65.

1,2,5-Trimethyl-4-ethylaminopiperidine (VII). 8.3 g of the 1,2,5-trimethyl-4-ethyliminopiperidine described above was dissolved in 10 ml of absolute alcohol and reduced with hydrogen and a platinum catalyst. Hydrogen was absorbed very slowly during the first 15-20 minutes, after which it sped up considerably, 1200 ml of hydrogen being absorbed during 1.5 hours. After hydrogenation slowed down sharply, some more catalyst was added, and hydrogenation was continued for another hour. After the catalyst had been filtered out and the alcohol driven off the hydrogenation product was distilled in vacuo. This yielded 5 g of 1,2,5-trimethyl-4-ethylaminopiperidine

(VII) as a colorless liquid with a strong amine odor. B.p. 83-84° at 9 mm.

n_D^{20} 1.4604; d_4^{20} 0.8732: MR_D found 53.45; calculated 53.72.

4.964 mg substance: 12.580 mg CO_2; 5.785 mg H_2O. 3.520 mg substance: 9.115 mg CO_2; 4.140 mg H_2O. Found %: C 70.77, 70.67; H 13.10, 13.15. $C_{10}H_{22}N_2$. Calculated %: C 70.53; H 13.02.

The picrate of 1,2,5-trimethyl-4-ethylaminopiperidine was produced as soon as the base was added to an alcoholic solution of picric acid. It is very poorly soluble in hot alcohol. The m.p. of the picrate was 218° after double recrystallization from 50% alcohol.

1,2,5-Trimethyl-4-phenyliminopiperidine (VI). A mixture of 25 g of 1,2,5-trimethyl-4-piperidone and 25 g of aniline was heated to 85-90° on a water bath for 4.5 hours. Then the mixture was heated in a 100-mm vacuum for 3 hours, about 1 g of water being driven off. Vacuum fractionation of the reaction products in a current of anhydrous nitrogen yielded 37 g of a mixture of the unreacted aniline and piperidone (b.p. 75-78° at 10 mm) plus 7.5 g of 1,2,5-trimethyl-4- phenyliminopiperidine (VI) with a b.p. of 131-132° at 5 mm.

n_D^{20} 1.5432; d_4^{20} 0.9892. MR_D found 68.95; calculated 67.67.

10.064 mg substance: 1.150 ml N_2 (24°, 752 mm). 9.600 mg substance: 1.091 ml N_2 (22°, 751 mm). Found %: N 12.99, 13.00. $C_{14}H_{20}N_2$. Calculated %: N 12.95.

When we tried to secure the picrate by reacting the reaction product with an alcoholic solution of picric acid we got the picrate of 1,2,5-trimethylpiperidone, with a m.p. of 159-161°, which exhibited no depression when mixed with a known sample.

The synthesized 1,2,5-trimethyl-4- phenyliminopiperidine is hardly hydrogenated at all with Pt, Pd, and Ni catalysts. We therefore effected hydrogenation with metallic sodium in an absolute alcohol solution.

1,2,5-Trimethyl-4-phenylaminopiperidine (VIII). 5 grams of 1,2,5-trimethyl-4 - phenyliminopiperidine was dissolved in 80 ml of alcohol, and 8 g of metallic sodium was added in small bits to the continuously stirred solution. After all the sodium had dissolved, the solution was neutralized with 70 ml of dilute hydrochloric acid (1:1), the precipitated sodium chloride being filtered out and the alcohol driven off, while alkali was added to the aqueous solution of the amine hydrochloride until the free base separated as a separate layer. The free base was extracted with ether, dried with a caustic alkali, and fractionated in vacuo. This yielded 3 g of 1,2,5-trimethyl-4-phenylaminopiperidine (VIII) as a viscous, thick, colorless oil with a faint amine odor. B.p. 138-139° at 4 mm; 150-151° at 6.5 mm.

n_D^{20} 1.5472; d_4^{20} 0.9668· MR_D found 71.64. Calculated 68.59.

3.597 mg substance: 10.065 mg CO_2; 3.270 mg H_2O. 6.605 mg substance: 18.450 mg CO_2; 5.945 mg H_2O. Found %: C 76.35, 76.23; H 10.17, 10.07. $C_{14}H_{22}N_2$. Calculated %: C 77.01; H 10.16.

1,2,3,6-Tetramethyl-4-piperidone (XIII). 40 g of the 1,2,3,6-tetramethyl-4-piperidone described previously [2], prepared by reacting methylamine with 5-methyl-1,5-heptadien-4-one and therefore containing 1,2,3,6-tetramethyl-4-methyliminopiperidine as an impurity, was dissolved in 200 ml of water, and the solution was refluxed at 80-90° for 5 hours. Heating results in the partial separation of the piperidone as a layer, which redissolves as the reaction mixture cools. After salting out with potash, the product was extracted with ether, dried with calcined potash, and fractionated in vacuo. This yielded 34.8 g of pure 1,2,3,6-tetramethyl-4-piperidone (XIII) with a b.p. of 86-88° at 7.5 mm.

n_D^{20} 1.4680; d_4^{20} 0.9499. MR_D found 45.43; calculated 45.51.

9.337 mg substance; 0.746 ml N_2 (24°, 733 mm). 6.445 mg substance: 0.529 ml N_2 (25°, 733 mm). Found %: N 8.86, 9.07. $C_9H_{17}ON$. Calculated %: N 9.02.

1,2,3,6-Tetramethyl-4-methyliminopiperidine (IX). We took 30 g of 1,2,3,6-tetramethyl-4-piperidone (b.p. 86-88° at 7.5. mm; n_D^{20} 1.4680), chilled it with ice and salt, and then dissolved 11.5 g of gaseous methylamine (a 90% excess) in it. The mixture was then heated to 90° in a metallic ampoule for 4.5 hours. After the excess methylamine had been driven off and the overhead fractions, consisting mainly of water (2.1 g) had been distilled, distillation in a current of anhydrous nitrogen yielded 29.5 g of a product with a b.p. of 90.5-93° at 7.5 mm; n_D^{19} 1.4800. Triple distillation in vacuo in a current of anhydrous nitrogen yielded 11.5 g of 1,2,3,6-tetramethyl-4-methyliminopiperidine (IX) as a colorless mobile liquid with the disagreeable strong odor of a base. B.p. 90-91° at 7.5 mm.

n n_D^{20} 1.4818; d_4^{20} 0.9140. MR_D found 52.47; calculated 52.80.

5.680 mg substance: 0.794 ml N_2 (22°, 749 mm). 5.470 mg substance: 0.761 ml N_2 (21°, 750 mm).
Found %: N 15.94, 15.94. $C_{10}H_{20}N_2$. Calculated %: N 16.65.

When we tried to secure the picrate by using an alcoholic solution of picric acid, we got the picrate of 1,2,3,6-tetramethylpiperidone, with a m.p. of 146-148°, which exhibited no depression when mixed with a known sample.

1,2,3,6-Tetramethyl-4-methylaminopiperidine (XI). 5.2 grams of 1,2,3,6-tetramethyl-4-methyliminopiperidine (b.p. 90-91° at 7.5 mm; n_D^{20} 1.4818) was dissolved in 12 ml of alcohol, and the solution was agitated in hydrogen under pressure with a platinum catalyst. It took 3 hours for the absorption of hydrogen to start, the hydrogen absorbed totalling 740 ml. The catalyst was filtered out, the solvent driven off, and the hydrogenation product distilled twice in vacuo. This yielded 2.5 g of 1,2,3,6-tetramethyl-4-methylaminopiperidine (XI) as a colorless liquid with the odor of a base. B.p. 76-77° at 4.5 mm.

n_D^{25} 1.4720; d_4^{25} 0.8971. MR_D found 53.16; calculated 53.72.

3.263 mg substance: 8.450 mg CO_2; 3.795 mg H_2O. 4.950 mg substance: 12.796 mg CO_2; 5.730 mg H_2O.
Found %: C 70.67, 70.51; H 13.10, 12.95. $C_{10}H_{22}N_2$. Calculated %: C 70.53; H 13.02.

The dipicrate of 1,2,3,6-tetramethyl-4-methylaminopiperidine was slightly soluble in alcohol. M.p. 232-233° with decomposition (from 50% alcohol).

6.145 mg substance: 9.445 mg CO_2; 2.435 mg H_2O. 4.296 mg substance: 6.580 mg CO_2; 1.685 mg H_2O.
4.765 mg substance: 0.756 ml N_2 (23°, 729 mm). 4.410 mg substance: 0.696 ml N_2 (23°, 730 mm).
Found %: C 41.94, 41.80; H 4.41, 4.39; N 17.55, 17.48. $C_{22}H_{38}O_{14}N_8$. Calculated %: C 42.04; H 4.49; N 17.83.

1,2-Dimethyl-4-ketodecahydroquinoline (XVII). The preparation of 1,2-dimethyl-4-ketodecahydroquinoline prepared with a great excess of methylamine (sevenfold excess), which grew very dark when stored for a long time (2 years) and turned into a thick black mass, was double-distilled again in vacuo. Distillation yielded 3.0 g of pure 1,2-dimethyl-4-ketodecahydroquinoline (XVII) as a colorless liquid that was stable in storage, with a b.p. of 111-112° at 5 mm.

n_D^{20} 1.4970; d_4^{20} 1.0111. MR_D found 52.46; calculated 52.55.

4.440 mg substance: 0.303 ml N_2 (23°, 723 mm). 3.410 mg substance: 0.239 ml N_2 (23°, 723 mm).
Found %: N 7.49, 7.69. $C_{11}H_{19}ON$. Calculated %: N 7.77.

1,2-Dimethyl-4-methyliminodecahydroquinoline (X). 14 grams of 1,2-dimethyl-4-keotodecahydroquinoline (b.p. 111-112° at 5 mm) was chilled with an ice-salt mixture, after which it dissolved 6.7 g of gaseous methylamine (some 200% excess). The solution was heated to 80-90° in a metallic ampoule for 6 hours. Double fractionation of the reaction product in vacuo in a current of nitrogen yielded 2.5 g of 1,2-dimethyl-4-methyliminodecahydroquinoline (X), with a b.p. of 112-113° at 4 mm.

n_D^{20} 1.5095; d_4^{20} 0.9809. MR found 59.20; calculated 58.83.

5.290 mg substance: 0.588 ml N_2 (23°, 761 mm). 7.195 mg substance: 0.794 ml N_2 (23°, 761 mm).
Found %: N 12.84, 12.74. $C_{12}H_{22}N_2$. Calculated %: N 14.42.

Analysis showed that the synthesized 1,2-dimethyl-4-methyliminodecahydroquinoline was not wholly pure, containing a trace of the initial 1,2-dimethyl-4-ketodecahydroquinoline.

When 1,2-dimethyl-4-methyliminodecahydroquinoline was mixed with an alcoholic solution of picric acid, the picrate was formed at once, settling out as an oil and crystallizing when the solution was heated. When the picrate was recrystallized from alcohol, part of it remained undissolved and was set aside. The picrate crystals that settled out of the solution had an m.p. of 158° and exhibited no depression when mixed with the previously prepared picrate of 1,2-dimethyl-4-ketodecahydroquinoline (m.p. 157-157.5°).

The slightly soluble picrate was recrystallized, after which its melting point was 174-175°; its composition was likewise that of the picrate of 1,2-dimethyl-4-ketodecahydroquinoline.

4.370 mg substance: 0.490 ml N_2 (22°, 752 mm). 5.677 mg substance: 0.642 ml N_2 (22°, 752 mm).
Found %: N 12.84, 12.95. $C_{17}H_{22}O_8N_4$. Calculated %: N 13.69.

1,2-Dimethyl-4-methylaminodecahydroquinoline (XII). 7 grams of 1,2-dimethyl-4-methyliminodecahydroquinoline was dissolved in 15 ml of alcohol, and the solution was agitated with a platinum catalyst in hydrogen under pressure. Hydrogen began to be absorbed after 2 hours had passed, being slow at first, but later speeding up considerably. A total of 840 ml of hydrogen was absorbed in 40 minutes. The catalyst was then filtered out, the solvent driven off, and the reaction product fractionated in vacuo. This yielded 4.0 g of 1,2-dimethyl-4-methylaminodecahydroquinoline (XII) as a colorless liquid that rapidly turned pink in storage. B.p. 113-115° at 6.5 mm.

n_D^{21} 1.4985.

3.466 mg substance: 9.335 mg CO_2; 3.675 mg H_2O. 3.399 mg substance: 9.155 mg CO_2; 3.630 mg H_2O. Found %: C 73.50, 73.50; H 11.86, 11.95. $C_{12}H_{24}N_2$. Calculated %: C 73.41; H 12.33.

The dipicrate of 1,2-dimethyl-4-methylaminodecahydroquinoline settled out as an oil when the base was mixed with a saturated alcoholic solution of picric acid and slowly crystallized. Recrystallization from 50% alcohol yielded a picrate with an m.p. of 214-216° (turning dark at about 200°).

4.150 mg substance: 0.613 ml N_2 (22°, 752 mm). 4.542 mg substance: 0.679 ml N_2 (22°, 752 mm). Found %: N 16.91, 17.12. $C_{24}H_{30}O_{14}N_8$. Calculated %: N 17.12.

1,2,5-Trimethyl-6-ethyl-4-piperidone (XIV). 5 grams of the previously described [3] 1,2,5-trimethyl-6-ethyl-4-piperidone (b.p. 74-76° at 3 mm; n_D^{20} 1.4712, and b.p. 76-78°; 3 mm; n_D^{20} 1.4743), produced with a large excess of methylamine and containing 1,2,5-trimethyl-6-ethyl-4-methyliminopiperidine as an impurity, was mixed with 25 ml of water, and the mixture was vigorously stirred for 6 hours at 85-90°. After salting out with potash, the base was extracted with ether, dried with potash, and distilled in vacuo. Double distillation yielded 3.5 g of pure 1,2,5-trimethyl-6-ethyl-4-piperidone (XIV) as a colorless, mobile liquid with the odor of a base. B.p. 84.5-96° at 7 mm.

n_D^{20} 1.4682; d_4^{20} 0.9502. MR_D Found 49.54; Calculated 50.13.

6.730 mg substance: 0.509 ml N_2 (23°, 738 mm). 7.290 mg substance: 0.554 ml N_2 (23°, 738 mm). Found %: N 8.47, 8.51. $C_{10}H_{19}ON$. Calculated %: N 8.28.

1 2--Dimethyl-6-ethyl-5-propyl-4-piperidone (XV). 6 grams of the previously described [2] 1,2-dimethyl-6-ethyl-5-propyl-4-piperidone, synthesized with a large excess of methylamine and containing the imino derivative as an impurity (b.p. 81-83° at 2.5 mm; n_D^{20} 1.4682), was dissolved in 40 ml of 7% hydrochloric acid. The solution was heated for 5 hours to 80-90°, after which the base was recovered from the solution by adding a solid alkali, extracting with ether, and drying the ether solution with magnesium sulfate. After the ether had been driven off, the base was double-distilled in vacuo, yielding 5.1 g of pure 1,2-dimethyl-6-ethyl-5-propyl-4-piperidone (XV) as a colorless, mobile liquid with a b.p. of 122-124° at 13 mm.

n_D^{20} 1.4684; d_4^{20} 0.9285. MR_D found 59.12; calculated 59.37.

5.187 mg substance: 0.327 ml N_2 (23°, 755 mm). 7.580 mg substance: 0.474 ml N_2 (24°, 749 mm). Found %: N 7.22, 7.08. $C_{12}H_{23}ON$. Calculated %: N 7.10.

1,2,7-Trimethyl-4-ketodecahydroquinoline (XVI). 8 grams of the previously described [2] 1,2,7-trimethyl-4-ketodecahydroquinoline (b.p. 123.5° at 4 mm; n_D^{20} 1.4913), prepared with a large excess of methylamine and containing the imino derivative as an impurity, was dissolved in 50 ml of 7% hydrochloric acid, and the solution was heated to 85-90° for 6 hours. The free base was recovered by adding alkali, extracting with ether, drying with magnesium sulfate and double-distillation in vacuo. This yielded 4.4 g of pure 1,2,7-trimethyl-4-ketodecahydroquinoline (XVI) with a b.p. of 121-123° at 6 mm.

n_D^{20} 1.4927; d_4^{20} 0.9932. MR_D found 57.11; calculated 57.17.

3.305 mg substance: 0.220 ml N_2 (22°, 728 mm). 4.790 mg substance: 0.313 ml N_2 (22°, 733 mm). Found %: N 7.38, 7.29. $C_{12}H_{21}ON$. Calculated %: N 7.17.

SUMMARY

When γ-piperidones are heated with primary amines (methylamine, ethylamine, and aniline), the 4-iminopiperidines are produced: they are recovered in the pure state in some instances. When the 4-iminopiperidines are heated with water or dilute hydrochloric acid, they are readily hydrolyzed, yielding

the initial γ-piperidones, while hydrogenation converts them into the respective 4-aminopiperidines.

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CATALYTIC CONDENSATION OF ALCOHOLS WITH KETONES

I. CONDENSATION OF METHANOL WITH ACETONE

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There is an extensive literature on the condensation of ketones in the homogeneous phase, resulting in the formation of mesitylene, isophorone, xylitone, their analogs, their higher homologs, and other cyclic sybstances. No work has been done at all on the heterogeneous catalytic condensation of ketones. Nothing is known of the catalytic condensation of a mixture of alcohols and ketones in the heterogeneous phase. The only paper we have is one by Reckleben and Scheiber [1], who secured hexamethylbenzene from a mixture of methanol and acetone over alumina. Our endeavor to reproduce the results of these authors met with no success. No hexamethylbenzene was secured at all, the oily condensate layer containing appreciable quantities of phenols, which Reckleben and Scheiber did not secure. We assumed that so great a discrepancy in the course of the process must be due mainly to the nature of the catalyst. Subsequent experiments fully confirmed this assumption. The alumina we used, which came from the Central Chemical Supply Board, produced phenols at 400°, while the alumina supplied by the Kahlbaum firm yielded nothing but hexamethylbenzene (10-12%) under the same conditions. At our request, both samples were analyzed in the X-ray laboratory of the Institute of Applied Chemistry. Traces of Na and Mg were found in both samples, the German sample also containing copper, while the native sample contained iron and silicon. Assuming that the formation of phenols was caused by the presence of iron, we added the latter to the German sample of Al_2O_3 and actually secured phenols instead of hexamethylbenzene. This process seemed to us to be worthy of further study, which we therefore undertook.

To determine the optimum conditions for the formation of phenols, an equimolecular mixture of methanol and acetone was passed over Al_2O_3 containing different percentages of iron at various temperatures and volumetric flow rates. The effect of the iron content was studied at 410-420° and a rate of flow of 8-8.5 ml of the initial mixture per hour The phenol yield proved to be a maximum abo ve catalysts containing 10-15% of iron, so that we chose an Al_2O_3 catalyst containing 10% Fe for all our subsequent research The following were found to be the conditions required for optimum phenols yields from a methanol-acetone mixture: an Al_2O_3 catalyst containing 10% Fe at 400-410° and a flow rate of 8-8.5 ml of the mixture per hour over 100 ml of the catalyst. This yielded a two-layer condensate, the upper, oily layer containing the phenols, while the lower one consisted mainly of a methanol-acetone mixture with other reaction products of a nonphenolic nature. The phenol yield totaled 6.5% of the initial mixture or 8.9% of the condensate. The yield of the neutral oil was 7.9% of the initial mixture and 10.8% of the condensate.

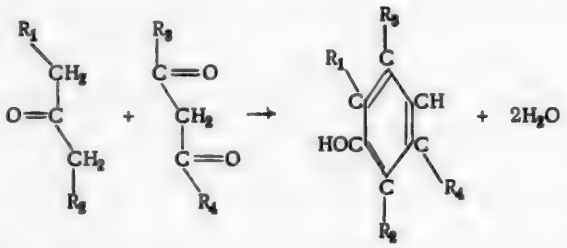
After the phenol layer had been separated, it was fractionated into a colum n with an efficiency of 25 theoretical trays, the phenols being identified in each fraction by the Steinkopf and Hopner [2] or the Holzman and Pilat method [3], involving their conversion into the respective aryl glycolic acids by means of monochloroacetic acid and solid sodium hydroxide. In some instances the production of the aryl glycolic acids was preceded by the separation of the phenols by the Bruckner method [4], involving the fractional cleavage of the phenolsulfonic acids We have isolated and identified the following phenols: phenol, m-cresol, 2, 5-dimethylphenol, and 3, 5-dimethylphenol. We did not explore the higher phenols. Most of the residual neutral oil consisted of various ketones. Repeated careful fractionation resulted in the isolation and identification of methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, mesityl oxide, and phorone.

The ketones are probably intermediates in the formation of the phenols. There are three possible ways in which phenols can be formed from mixtures of alcohols and ketones: 1) closing long carbon chains; 2) via the formation of isophorone; and 3) via the condensation of the ketones with β-diketones or β-keto-aldehydes. In this case, it seemed to us that the last of these was most likely, and this was confirmed by our results. The condensate contained no alcohols besides the initial methanol. Isophorone can hardly be an intermediate compound, inasmuch as only 3, 5-dimethylphenol was secured when the phenols were produced via isophorone by

the Ipatyev method [5], whereas we secured a complex mixture of phenols. These latter were produced only from a methanol-acetone mixture, neither methanol nor acetone giving rise to any phenols by itself, as was proved by special tests. The possibility of producing phenols by condensing ketones with diketones was also demonstrated experimentally. In our effort to establish the possible mechanism of the condensation of methanol and acetone, resulting in the formation of various phenols, we likewise condensed methanol with diacetone alcohols, mesityl oxide, and phorone, i.e., with the condensation products of acetone itself. In every instance the phenol yield was extremely low, never exceeding 2-3%, thus proving that these compounds could not be intermediates in the production of the phenols from methanol and acetone. The low yield of phenols secured in these condensations may be attributed to the partial reversible decomposition of the products into acetone, which is then converted with the methanol into phenols. We assumed that under our experimental conditions the phenols are formed via the intermediate formation of β-diketones or β-keto-aldehydes, which are themselves unstable thermally, so that they are not found in the end products. Schematically, the initial stages of the process should proceed as follows:

$$CH_3OH \rightarrow CH_2O + H_2O$$
$$CH_3COCH_3 + CH_2O \rightarrow CH_3-CO-CH_2-CH_2OH$$
$$CH_3-CO-CH_2-CH_2OH \rightarrow CO_3-CO-CH_2-CHO + H_2.$$

There is no doubt about the first stage, since the condensates always contain formaldehyde. That a ketol was produced was not established directly, but when ethyl alcohol was condensed with acetone, we proved that a decomposition product of the ketol was present – we secured ethylideneacetone. Further condensation of the ketones with di- or aldoketones yields phenols, the general pattern of their formation being as follows:



R_1, R_2, R_3, and R_4 may be hydrogen atoms or aromatic radicals. As a result, we secure all the experimentally established phenols. The process involves the splitting out of water and the dehydrogenation of the intermediate products, as is evidenced by the results of the gas analyses, which indicate a high percentage of hydrogen (as much as 50%) in the reaction gas. We believe that our investigation may throw some light upon the mechanism involved in the formation of phenols during the destructive distillation of wood.

EXPERIMENTAL

The catalytic heterogenous condensation of methanol and acetone yielded a two-layer liquid condensate; the upper layer was a dark oil, while the lower layer was aqueous, consisting of the unreacted initial substances plus other products. The phenols were extracted from the oily layer by repeated extraction with 10% NaOH. The resultant phenolates were extracted with ether to free them of the neutral oils that had been partially entrained with the alkali. When the phenolates were decomposed with dilute H_2SO_4, the phenols separated out as oils or crystalline products. The latter were filtered out, and the filtrate was re-extracted with ether. After the ether solution had been dried and the ether driven off, we got a mixture of phenols, which was then fractionated. The neutral part of the condensate was processed similarly before being fractionated. The results of this preliminary treatment of the products are given in Table 1.

Analysis of the phenols. Of the numerous methods of analyzing the phenols described in the literature, we chose the method of identification given by Steinkopf and Hopner [2] and Holzman and Pilat [3], as the simplest and most convenient. In some instances, as stated above, we used the method of first separating the phenols given by Bruckner [4]. Analysis indicated that the crystalline product secured was 3, 5-dimethylphenol. Recrystallization and sublimation yielded elongated acicular crystals with an m.p. of 66-68° (68° in the literature) and a b.p. of 219° (219.5° in the literature). Found: M 122, 123.4. $C_8H_{10}O$. Calculated: M 122.

TABLE 1

	Initial Mixture	Condensate		Lower layer		Phenols			Neutral oil
		Total	Upper layer / Lower layer	Driven off at 54-80°	Water	Total	Crystals	Oil	
Grams	2310	1675	955/720	1182	88	147.8	11.8	136	189
% of condensate	–	–	57/43	70.3	5.2	8.8	0.7	8.1	11.3
% of the initial mixture	–	72.5	41.2/31.3	51.3	3.8	6.4	0.5	5.9	8.2

We prepared the tribromide, which had an m.p. of 162-164° after three recrystallizations (the literature gives 163°).

Condensation with monochloroacetic acid and sodium hydroxide yielded an aryl glycolic acid with an m.p. of 85-86°, representing 3,5-xylenoxyacetic acid.

Found %: C 66.32, 66.5: H 6.7, 6.9. $C_{10}H_{12}O_3$. Calculated %: C 66.66; H 6.7.

The phenolic oil was distilled with a dephlegmator, a product that boiled continuously from 175-233°. The high-boiling residue represented 30% by weight of the phenolic oil. It apparently contained extremely complicated phenols, which we did not analyze any further. The product, with a b.p. of 175-233°, was repeatedly fractionated, all the narrower fractions being collected (Table 2).

TABLE 2

Fraction No.	Temperature	(g)	(%)
1	178-182°	5.5	6.1
2	182-205	9.4	10.4
3	205-210	10.2	11.3
4	210-216	17.0	13.9
5	216-225	21.0	23.3
6	225-230	17.1	19.0
	Residue, losses	9.8	11.0

The first fraction was condensed with monochloroacetic acid and sodium hydroxide. As the solution was chilled, the slightly soluble sodium salt settled out. This yielded an arylglycolic acid, with an m.p. of 97-99°, which is the melting point of phenoxyacetic acid. Found %: C 63.0, 62.96; H 5.35, 5.56. $C_8H_8O_3$. Calculated %: C 63.13; H 5.3.

The filtrate contained the readily soluble sodium salt of m-cresoxyacetic acid, with an m.p. of 100-102° (the literature gives 103°).

Found %: C 64.88, 64.75; H 6.39, 6.27. $C_9H_{10}O_3$. Calculated %: C 65.03; H 6.07.

The second fraction was processed like the first one. The precipitated arylglycolic acids were dissolved in hot benzene, the crystals that settled out being filtered out (the operation being repeated several times) and then recrystallized four times from alcohol. The resultant product had an m.p. of 96-98°. Its mixed melting point confirmed the presence of phenoxyacetic acid. An acid with an m.p. of 84-86°, corresponding to 3,5-dimethylphenoxyacetic acid, was recovered from the filtrate (the literature gives the m.p. as 86°).

The third fraction was also condensed with monochloroacetic acid and sodium hydroxide. The appropriate processing yielded a mixture of arylglycolic acids, which could not be separated by fractional crystallization. The fourth, fifth and sixth fractions were first separately processed as specified by Bruckner. The ether extracts of the aqueous distillates of all three of the initial fractions, collected at the same cleavage temperatures of the phenolsulfonic acids, were combined and dried. The phenols were isolated after the ether had been driven off. The results of our cleavage of the phenolsulfonic acids (50 g of phenol) are given in Table 3.

In every instance, a product that congealed into a colorless oil passed over up to 107°. Processing it in the usual manner yielded an acid with an m.p. of 84-86°, corresponding to 3,5-dimethylphenoxyacetic acid (the literature gives its m.p. as 86°). We were unable to isolate any individual products from the 107-115° fraction. The 115-119° fraction is the principal fraction, containing 23% by weight of sulfonated phenols. Processing it with twice its weight of monochloroacetic acid and sodium hydroxide yielded two acids: m-cresoxyacetic, benzene-soluble, with an m.p. of 102-103°, and 2,5-dimethylphenoxyacetic, soluble in petroleum ether, with an m. p. of 116-118° (the literature gives its m.p. as 118°). Elementary analysis of the latter acid yielded the following results:

TABLE 3

Fraction No.	Cleavage temperature	Phenol yield, grams	% of the initial phenol
1	up to 107°	6.2	12.4
2	107 - 115	3.7	7.4
3	115 - 119	11.5	23
4	120 - 125	6.6	13.2
5	125 - 136	5.4	10.8
	Losses	16.6	32.2

Found %: C 66.08, 66.35; H 6.9, 6.8; $C_{10}H_{12}O_3$. Calculated %: C 66.6; H 6.7.

The 120-125° fraction was converted into arylglycolic acids, the mixture yielding 0.5 g of a substance with an m.p. of 114-116°, which probably was 2,5-dimethylphenoxyacetic acid, which had been found in the preceding fraction.

Only an approximate answer can be given to the problem of the quantitative content of the individual phenols. The yields of the arylglycolic acids averaged 70-75% of the theoretical. The yields of the phenols after the sulfonic acids had been cleaved were about 76% of the original. The unavoidable losses in the recrystallization of small quantities of substances totaled 15-20%. The figures listed in Table 4 are of significance only for a comparative estimate of the results secured.

TABLE 4 Total Content of Individual Phenols

No.	Individual phenols	% of phenols
1	Phenol	1.2
2	m-Cresol	3.4
3	2,5-Dimethylphenol	6.1
4	3,5-Dimethylphenol	8.8
5	Phenols with b.p. >230°	40.0

Analysis of neutral products. This included an investigation of the lower, aqueous layer of the condensate, which boiled in the 54-80° range, and an investigation of the alkali-insoluble neutral oil. We managed to isolate 12 g of methyl ethyl ketone, with a b.p. of 78 - 80°, from the mixture of unreacted methanol and acetone by repeated fractionation.

TABLE 5

Ketone	Ketone constants			Semicarbazone melting point	Analysis of semicarbazones	
	Boiling point	d_4^{20}	n_D^{20}		% Calculated	% Experimental
Methyl ethyl ketone						
Our data	78 - 80°	0.8062	1.3827	134 - 136°	32.53	32.79; 32.91
Figures in the literature	80	0.805	1.3791	136		
Diethyl ketone [1]						
Our data	102	0.8151	1.3924	137 - 139	29.37	29.51
Figures in the literature	102	0.81425	1.3927	138 - 139		
Methyl isobutyl ketone						
Our data	117.5	0.8041	1.4070	130 - 132	27.75	26.4; 26.21
Figures in the literature	116.8	0.8008	1.3959	134		
Mesityl oxide						
Our data	128 - 130	0.8690	1.4428	164 (with decomposition)	27.10	27.24; 27.48
Figures in the literature	130	0.8650	1.4439	164		
Phorone [2]						
Our data	M.p. 25.5 - 26.5	—	—	—	—	—

[1] 2,4-Dinitrophenylhydrazone — m.p. 152-153° (the literature gives 156°).

[2] Found %: C 78.01, 78.38; H 10.26, 10.41. $C_9H_{14}O$. Calculated %: C 78.26; H 10.15.

Analysis of the oily product indicated that 43.5% of it had a b.p. in excess of 200°, constituting a complicated mixture of saturated and unsaturated carbonyl compounds. The product collected up to 220° (96 g) was rectified into a Todd-type column [6], with an efficiency of 25 theoretical trays. Carbonyl groups were qualitatively identified in all the collected fractions. We isolated the following individual ketones: 1) diethyl ketone, 2) methyl isobutyl ketone, 3) mesityl oxide, and 4) phorone. The characteristics of the substances recovered are listed in Table 5.

Analysis of gaseous products. At optimum conditions for the phenol yield the gases had the following composition: 42% H_2, 10.5% CO_2, 3.5% CO, 5% C_nH_{2n} hydrocarbons, 33% C_nH_{2n+2} hydrocarbons, 6% residue.

SUMMARY

1. A mixture of methanol and acetone passed over Al_2O_3 + 10% Fe_2O_3 at 400° yields a two-layer condensate containing 8.8% of phenols. Alumina containing no iron – like the individual methanol or acetone – produces no phenols. The variation of the phenol yield with the per cent of iron in the catalyst has been determined.

2. The phenolic portion of the condensate has been found to contain phenol, m-cresol, and 2,5- and 3,5-dimethylphenols.

3. The nonphenolic part of the condensate contains methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, mesityl oxide, and phorone.

4. The most probable mechanism for the formation of phenols, via β-diketones or β-keto-aldehydes, is proposed.

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CATALYTIC CONDENSATION OF ALCOHOLS WITH KETONES

II. CONDENSATION OF METHANOL WITH METHYL ETHYL KETONE, ETHYL ALCOHOL WITH ACETONE, AND ACETONE WITH ACETYLACETONE

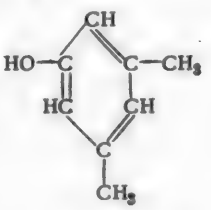
B. N. Dolgov and I. N. Samsonova

In our preceding report we described the process we have discovered for producing phenols by condensing methanol with acetone at 410° over an alumina catalyst containing iron. On the assumption that this was a general reaction, we undertook further research with the objective of demonstrating the applicability of these processes to other systems, and of confirming the correctness of the schema proposed by us for the formation of the phenols via β-diketones or β-keto-aldehydes in other instances. As will be seen below, our assumptions have been largely confirmed. Condensation of methanol with methyl ethyl ketone has yielded o-cresol mixed together with higher phenols, which were not investigated any further.

Condensing ethyl alcohol with acetone yielded 3,5-dimethylphenol as the sole phenol product, probably as follows:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$
$$CH_3COCH_3 + CH_3CHO \rightarrow CH_3COCH_2CHOHCH_3$$
$$CH_3COCH_2CHOHCH_3 \rightarrow CH_3COCH_2COCH_3 + H_2$$

$$CH_3COCH_2COCH_3 + CH_3COCH_3 \rightarrow 2H_2O +$$



The correctness of this schema is likewise borne out by the fact that the resultant condensate contained some ethylidene ketone, a product of the thermal decomposition of the β-ketol [1]

$$CH_3COCH_2CHOHCH_3 \rightarrow CH_3COCH{=}CHOH + H_2O.$$

When ethyl alcohol was condensed with acetone, no higher ketones were found in the nonphenolic part of the condensate, which is why no other phenols could be formed, according to the proposed schema.

When acetone was condensed with acetylacetone in order to check this schema, we secured the expected 2,5-dimethylphenol. All the results described below were secured under the optimum conditions (400-410°), with 8 ml of the initial mixture passing over the Al_2O_3 + 10% Fe_2O_3 catalyst per hour.

EXPERIMENTAL

1. Methanol-methyl ethyl ketone system. The two-layer condensate collected in numerous runs made under identical conditions was processed to separate the phenolic portion (cf Report I). The dried phenols (44 g) were rectified in a column with an efficiency of 25 theoretical trays, the following fractions being collection:

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[1] Claisen produced a β-ketol from acetone and acetaldehyde [1].

No.	Boiling point	Grams	Per cent
1	189 - 190°	2.5	5.7
2	205 - 216	0.4	0.9
3	216 - 218	2.5	5.7
4	218 - 225	4	9.1
	Above 225°	28.6	65.0
	Losses	6.0	13.6

All these fractions were analyzed for individual phenols by preparing the arylglycolic acids [2]. When the first fraction was condensed with monochloracetic acid and sodium hydroxide, we secured an arylglycolic acid with an m.p. of 150 - 152°, representing orthocresoxyacetic acid (this m.p. is given as 151 - 152° in the literature).

Found %: C 64.92; H 6.31. $C_9H_{10}O_3$. Calculated %: C 65.03; H 6.07.

When fractions 3 and 4 were allowed to stand in a freezing mixture, colorless crystals settled out, their m.p. being 80 - 81° after several recrystallizations.

Found %: C 79.27, 79.01; H 9.08, 8.99; M 131.1, 133.5. $C_9H_{12}O$. Calculated %: C 79.41; H 8.87; M 136.

These values are very close to the theoretical C and H content of methylethyl - or propylphenols. All our attempts to secure a crystalline arylglycolic acid from Fractions 3 and 4 met with failure, however. The residue, boiling over 225°, constituted 65% by weight of the total phenols. Nor were we able to secure crystalline arylglycolic acids from this residue. The percentage of hydroxyl groups in this residue was determined quantitatively. This was done by methylating part of the residue by the Heuser method [3], after which the methoxyl number was determined by the Viebock and Schupach method [4]. The hydroxyl percentage was found to be 12.6%. This indicated that the bulk of the phenols produced when methanol was condensed with methyl ethyl ketone consisted of high-boiling complicated phenols.

The neutral portion of the oil (80 g) was separated from the phenols and fractionated into a column. This yielded a series of fractions, each of which boiled in a wide temperature range. Analysis showed that none of them was an individual substance. Qualitative reactions indicated that the neutral oil was a complicated mixture of saturated carbonyl compounds together with the unreacted initial substances.

2. Ethyl alcohol - acetone system. An equimolecular mixture of rectified alcohol (94% ethyl alcohol) and acetone was passed over the catalyst at 400 - 410°. The resulting two - layer condensate was treated with an alkali solution to separate the phenols from the neutral reaction products. The phenols recovered by acidulating the alkaline solution were dried with calcined sodium sulfate and then distilled. Distillation of 25 g of phenols yielded the following fractions: 1) b.p. 215 - 218°, 6.5 g (27%); 2) 218 - 220°, 12 g (50 %); and 5.5 g (23%) residue and losses. The bulk of the phenols in this system boiled within the 215 - 220° range. Both of the fractions crystallized completely when allowed to stand in a freezing mixture. After the snow - white crystals had been recrystallized from alcohol, they had an m.p. of 66 - 68°. This yielded 12.8 g of the pure product, which proved to be 3, 5 - dimethylphenol upon analysis.

Found: M 121.8, 122.8. $C_8H_{10}O$. Calculated M 122.

Three grams of the crystals were condensed with 3 g of monochloroacetic acid and 3 g of sodium hydroxide. After the resultant arylglycolic acid had been recrystallized, it had an m.p. of 84 - 85° (the m.p. of 3, 5 - dimethylphenoxyacetic acid is 86°). Thus 3, 5 - dimethylphenol is the only phenol produced by condensing ethyl alcohol with acetone.

The lower, aqueous layer boiled in the 63 - 80° range and contained an unreacted mixture of ethyl alcohol and acetone. The neutral dephenolized portion of the oil distilled at 100 - 224° when rectified. Nine different fractions were collected, containing carbonyl compounds — ketones — plus aldehydes or keto - aldehydes in some instances. Redistillation of the 123 - 126° fraction yielded 4.2 g of ethylideneacetone:

B.p. 122-124°, d_4^{20} 0.8590, n_D^{20} 1.4373. Literature data: b.p. 124°, d_4^{20} 0.8560. n_D^{20} 1.4350.

A semicarbazide-semicarbazone of ethylideneacetone, with an m.p. of 124-126°, was prepared.

Found %: N 38.52, 39.01. $C_7H_{16}O_2N_6$. Calculated %: N 38.88.

Repeated fractionation of the 126-130° fraction yielded a substance with a b.p. of 127-128.5°, representing pure mesityl oxide (n_D^{20} 1.4442). The semicarbazone had an m.p. of 162-163°.

Found %: N 27.22; $C_7H_{13}N_3O$. Calculated %: N 27.10.

3. Acetone-acetylacetone system. An equimolecular mixture of the two reagents was passed over the catalyst at 400° at a rate of 8 ml per hour. The condensate was treated with alkali to recover the phenols as described above. The oily phenols thus recovered crystallized completely after distillation. Recrystallization from petroleum ether yielded snow-white crystals with an m.p. of 66-67°, which was that of the expected 3,5-dimethylphenol, m.p. 68°.

Found %: M 121.3, 123.1. $C_8H_{10}O$. Calculated: M 122.

Condensation with monochloroacetic acid and sodium hydroxide yielded an arylglycolic acid, the m.p. of which was 84-85.5° after two recrystallizations from alcohol (the literature gives this m.p. as 86°). Its mixed melting point with known 3,5-triphenoxyacetic acid exhibited no depression. As we expected, the principal product of the condensation of acetone with acetylacetone was 3,5-dimethylphenol.

SUMMARY

1. Condensing methanol with methyl ethyl ketone at 400° over Al_2O_3 containing added Fe_2O_3 yields some o-cresol plus a complicated mixture of higher phenols.

2. Condensing the ethyl alcohol-acetone system under the same conditions yields 3,5-dimethylphenol as the sole phenolic product.

3. Condensing acetone with acetylacetone, in order to check the hypothesis advanced to explain the formation of the phenols, yields the expected 3,5-dimethylphenol.

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THE REACTIONS OF ORGANOMERCURY COMPOUNDS WITH AMIDES OF FATTY ACIDS

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In our preceding paper [1] we described a reaction in which radicals were split off from complete organomercury compounds by heating them with succinimide. We found that the reaction occurs very readily, one radical being split off and the corresponding succinimidic mercury derivative being formed. We were interested in determining whether other acid amides would react like succinimide. We did this by running tests with acetamide and diacetamide. When diphenylmercury was heated to 141 - 145° with acetamide, we secured a nearly quantitative yield of phenylmercuryacetamide, benzene being evolved:

$$(C_6H_5)_2Hg + CH_3CONH_2 \rightarrow C_6H_6 + C_6H_5HgHNCOCH_3.$$

Ditolylmercury and di-*a*-naphthylmercury reacted similarly, but with much more difficulty. When diethylmercury was heated for a long time with acetamide, no ethane was split off nor was an acetamide derivative formed. Raising the experimental temperature above 150° caused thermal decomposition of the diethylmercury to set in without the latter reacting with the acetamide.

Diphenylmercury reacted in about the same conditions with diacetamide:

$$(C_6H_5)_2Hg + (CH_3CO)_2NH \rightarrow C_6H_6 + C_6H_5HgN(COCH_3)_2.$$

Like the acetamide, diacetamide did not react with diethylmercury.

The acetamide and diacetamide derivatives of an arylmercury compound and hydrochloric acid produce quantitative yields of the arylmercury chloride. Phenylmercury iodide was synthesized by reacting sodium iodide with phenylmercuryacetamide and phenylmercurydiacetamide.

The acetamide derivatives of p-tolylmercury and *a*-naphthylmercury yielded the respective symmetrical derivatives of a diarylmercury when reacted with sodium iodide in the same fashion.

EXPERIMENTAL

I Reactions of complete organomercury compounds with acetamide. The organomercury compounds were reacted with acetamide in reaction vessels heated on an oil bath. The constituents were reacted together in the molten state. The reactions lasted from 4 to 12 hours. No by-products or tarring was observed during the reactions. The experimental findings are listed in Table 1.

TABLE 1

Test No.	R_2Hg	Grams of R_2Hg used for the reaction	Grams of CH_3CONH_2 used for the reaction	Oil bath Temperature	RH yield		$RHgHNCOCH_3$ yield	
					Grams	Per cent	Grams	Per cent
1	$(C_6H_5)_2Hg$	3.6	1.3	140 - 145°	0.6	75.0	3.1	92.8
2	$(p\text{-}CH_3C_6H_4)_2Hg$	1.9	0.6	200 - 210	0.5	100.0	0.6	35.4
3	$(a\text{-}C_{10}H_7)_2Hg$ . .	2.9	6.0	140 - 145	0.6	74.1	0.6	25.0
4	$(C_2H_5)_2Hg$	4.9	2.2	140 - 150	–	–	–	–

Experiments 1 and 2 were performed in a round-bottomed flask with a sabre-shaped outlet tube, on which a small air-cooled condenser was mounted. During the reactions benzene (Test 1) and toluene (Test 2) condensed at the bend in the outlet tube. The benzene and toluene were identified by producing their nitro products. The benzene was nitrated to m-dinitrobenzene (m.p. 89°), and the toluene to 2, 4-dinitrotoluene (m. p. 70°). Their mixed melting points with the pure substances exhibited no depression.

Experiment 3 was performed in a large test tube. The naphthalene produced in the reaction was driven off with steam. The melting point of the naphthalene secured was 80°, exhibiting no depression when mixed with the pure product.

The reaction of diethylmercury with acetamide (Test 4) was performed in a round-bottomed flask fitted with a reflux condenser and connected to a gas buret. No ethane was evolved when the temperature of the oil bath was about 140°, the initial reagents being recovered from the reaction mixture. Prolonged heating (up to 35 hours) at temperatures in excess of 150° resulted in the partial thermal decomposition of the diethylmercury into ethane, ethylene, and metallic mercury. No ethylmercuryacetamide was found in the reaction products.

In every case the organomercury derivatives were recovered from the reaction mixture by extracting them repeatedly with boiling water. After the extract had been evaporated and cooled with water, the organomercury derivative of acetamide settled out as a white amorphous powder. This was followed by double recrystallization from benzene. Pure products were secured, their physical properties being listed in Table 2.

TABLE 2

Test No.	$RHgHNCOCH_3$	Melting point (from benzene)	Solubility		
			Cold water	Hot water	Benzene
1	$C_6H_5HgHNCOCH_3$	167 - 168°	Sparing	Low	Good
2	$p\text{-}CH_3C_6H_4HgHNCOCH_3$ . .	243 - 244	Sparing	Low	Good
3	$\alpha\text{-}C_{10}H_7HgHNCOCH_3$	199 - 203	Sparing	Low	Low

Phenylmercuryacetamide. 0.3604 g substance: 0.2604 g HgS. Found %: Hg 59.51. C_8H_9ONHg. Calculated %: Hg 59.77.

Tolylmercuryacetamide. 0.3124 g substance: 0.2070 g HgS. Found %: Hg 57.14. $C_9H_{11}ONHg$. Calculated %: Hg 57.38.

II. Reactions with HCl and NaI. The reactions were performed in a round-bottomed flask, fitted with a reflux condenser. Acetone was used as the solvent because of the low solubility of organomercury derivatives of acetamide in water. A sample of the test substance (0.05-0.2 g) was dissolved in boiling acetone, and then a solution of HCl (or NaI) in acetone was added. After boiling had proceeded for a short time, the excess solvent was driven off. The organomercury compound that settled out upon cooling was filtered out and dried. This was followed by recrystallization from benzene.

In every case the reaction products were identified by determining their melting points and their mixed melting points with the pure substances. The test results are listed in Table 3.

TABLE 3

No.	$RHgHNCOCH_3$	Reaction with HCl				
		Reaction product	Grams of initial substance used	Grams of product secured	% yield	Melting point
1	$C_6H_5HgHNCOCH_3$	C_6H_5HgCl	0.20	0.17	91.4	251°
2	$p\text{-}CH_3C_6H_4HgHNCOCH_3$ . . .	$p\text{-}CH_3C_6H_4HgCl$ . . .	0.25	0.23	98.7	233
3	$\alpha\text{-}C_{10}H_7HgHNCOCH_3$	$\alpha\text{-}C_{10}H_7HgCl$	0.15	0.12	85.7	189
No.	$RHgHNCOCH_3$	Reaction with NaI				
		Reaction product	Grams of initial substance used	Grams of product secured	% yield	Melting point
1	$C_6H_5HgHNCOCH_3$	C_6H_5HgI	0.06	0.06	90.2	271°
2	$p\text{-}CH_3C_6H_4HgHNCOCH_3$ . . .	$(p\text{-}CH_3C_6H_4)_2Hg$	0.10	0.05	92.5	238
3	$\alpha\text{-}C_{10}H_7HgHNCOCH_3$	$(\alpha\text{-}C_{10}H_7)_2Hg$	0.05	0.03	100	246

III. Reactions of diacetamide with diphenylmercury and diethylmercury. a) Reaction of diphenylmercury with diacetamide. The diacetamide was prepared by acetylating acetamide with acetic anhydride. 3.6 grams of diphenylmercury and 2.0 g of diacetamide were placed in a round-bottomed flask possessing a

sabre-shaped outlet tube. The reaction flask was heated to 150-165° for 4 hours on an oil bath. Benzene condensed at the bend of the outlet tube. The benzene weighed 0.6 g, representing 75% of the theoretical. Nitration with benzene yielded 0.8 g of m-dinitrobenzene with an m.p. of 89°. Its mixed melting point exhibited no depression. The phenylmercurydiacetamide was extracted from the reaction mixture with hot water and recrystallized twice from the latter. This yielded 0.35 g of the pure substance with an m.p. of 152-153°. The yield of phenylmercurydiacetamide was 35.7%.

Phenylmercurydiacetamide is a white crystalline substance, freely soluble in hot water and the customary organic solvents.

0.2032 g substance: 0.1251 g HgS. Found %: Hg 53.10. $C_{10}H_{11}O_2NHg$. Calculated %: Hg 53.12.

b) Reaction of phenylmercurydiacetamide with HCl. 0.21 gram of phenylmercurydiacetamide was dissolved in hot water, and an alcoholic solution of concentrated hydrochloric acid was added. Phenylmercury chloride was precipitated instantaneously. The precipitate was filtered out, dried, and recrystallized from benzene. This yielded 0.17 g of the substance, representing 100% of the calculated yield. M.p. 251°, exhibiting no depression with pure phenylmercury chloride.

c) Reaction of phenylmercurydiacetamide with KI. A large excess of a hot solution of KI was added to a hot aqueous solution of 0.13 g of phenylmercurydiacetamide. An abundant white precipitate of phenylmercury iodide settled out. The precipitate was filtered out, dried, and twice recrystallized from benzene. This yielded 0.13 g of pure phenylmercury iodide (93.5%), with an m.p. of 266°. Its mixed melting point exhibited no depression.

d) Reaction of diethylmercury with diacetamide. 1.5 gram of diacetamide and 4.3 g of diethylmercury were placed in a reaction flask fitted with a reflux condenser and connected to a gas buret. The mixture was heated to 150-160° (oil bath) for 4.5 hours. After the reaction was over, the unreacted initial substances were recovered from the reaction vessel.

SUMMARY

1. The reactions of acetamide and diacetamide with organomercury compounds have been investigated.

2. Diarylmercury derivatives react by splitting off one radical as a hydrocarbon and forming an arylmercuryacetamide or an arylmercurydiacetamide.

3. Diethylmercury does not react when heated with acetamide or diacetamide.

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THE REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH THIOSALICYLIC ACID AND THIOPHENOL

M. M. Koton

The author has previously shown [1] that diphenylmercury yields benzene and the corresponding organomercury derivatives when reacted with various organic acids, in accordance with the general equation (1):

$$(C_6H_5)_2Hg + RCOOH \rightarrow C_6H_6 + RCOOHgC_6H_5 \qquad (1)$$

the hydroxy acids being the most reactive. The author later showed [2] that various organomercury compounds (Ar_2Hg, Alk_2Hg, ArHgOAc, etc.) readily mercurate phenol in accordance with Equation (2):

$$R_2Hg + R'C_6H_4OH \rightarrow RH + R'C_6H_3(OH)HgR. \qquad (2)$$

The reactions of organomercury compounds that contain an SH group with derivatives of the phenols and acids follow a totally different course. When diphenylmercury is reacted with the thiophenols [3], metallic mercury settles out, and benzene, disulfides, and mercury thiophenolates are produced (3):

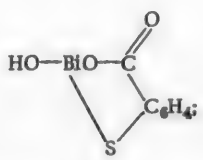
$$(C_6H_5)_2Hg + RC_6H_4SH \rightarrow Hg + C_6H_6 + (RC_6H_4S)_2Hg + (RC_6H_4S)_2. \qquad (3)$$

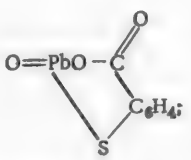
In the present paper we have made a study of the reaction of organometallic compounds with thiosalicylic and thioglycolic acids and have shown that mercury compounds of the RHgHal type, which do not react with the phenols at 150-175°, react readily with thiophenol at 130°. The following reactions were investigated: diphenylmercury with thioglycolic and thiosalicylic acids, RHgHal and R_2Hg with thiosalicylic acid, RHgHal with thiophenol, and $(C_6H_5)_3Bi$, $(C_6H_5)_4Pb$ and $(C_6H_5)_4Sn$ with thiosalicylic acid at 100-130°.

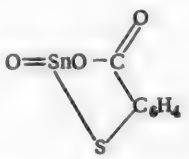
We know from the literature [4] that some RHgHal compounds react with thiosalicylic acid when an alcoholic alkali is present, yielding compounds of the $RHgSC_6H_4COOMe$ type, which possess strong antiseptic properties. When aromatic compounds of mercury, lead, tin and bismuth are reacted with thiosalicylic acid, hydrocarbons and the corresponding metallic derivatives of thiosalicylic acid are produced:

$$R_2Hg + 2HSC_6H_4COOH \rightarrow 2RH + Hg(SC_6H_4COOH)_2 \qquad (4)$$

The reaction takes place readily at 100-130°, 130° being required only in the case of tetraphenyllead. The stability of the metallic derivatives of thiosalicylic acid varies, mercuribisthiosalicylic acid, $Hg(SC_6H_4COOH)_2$, being the most stable compound. The lead, tin, and bismuth derivatives are readily hydrolyzed, yielding the basic salts:







In contrast to other organometallic compounds (Sn, Pb, and Bi), the aromatic compounds of mercury liberate metallic mercury when they are reacted with thiocarboxylic acids. The production of metallic mercury may be explained as an oxidation reaction of the thiosalicylic acid to diphenyldisulfodicarboxylic acid according to Equation (5):

$$R_2Hg + 2HSC_6H_4COOH \rightarrow Hg + 2RH + (HOOCC_6H_4S)_2, \qquad (5)$$

as well as the action of the mercuribisthiosalicylic acid, produced in Equation (4) with the solvent (alcohol), according to Equation (6):

$$Hg(SC_6H_4COOH)_2 + CH_3CH_2OH \rightarrow Hg + 2HSC_6H_4COOH + CH_3CHO. \quad (6)$$

When diphenylmercury is reacted with thioglycolic acid, much less metallic mercury is thrown down (19%) than in the reaction with thiosalicylic acid (63%), and we are unable to isolate a stable mercury derivative of thioglycolic acid. Other aryl compounds of mercury react with thiosalicylic acid like diphenylmercury, with the sole exception of dibenzylmercury, which yields R – R (dibenzyl) instead of an RH hydrocarbon. The RHgHal organomercury compounds react readily with thiosalicylic acid and thiophenol at 100-130° (Tables 2 and 3).

TABLE 1

Reaction of R_2Hg with Thiosalicylic and Thioglycolic Acids

Test No.	R_2Hg	Thio acid	t°	Time, hours	% metallic Hg	Per cent $Hg(SC_6H_4COOH)_2$ produced	Other reaction products
1	Diphenylmercury	Thioglycolic acid	100°	6	1.95	–	–
2	Diphenylmercury	" "	130	3	6.60	–	–
3	"	" "	130	6	19.00	–	–
4	"	Thiosalicylic acid	100	3	15.8	24.0	Benzene
5	"	" "	100	6	33.6	40.0	"
6	"	" "	130	3	35.4	36.0	"
7	"	" "	130	6	43.5	41.0	"
8	"	" "	130	6	3.5	74.0	"
9	"	" "	130	6	21.0	56.0	"
10	"	" "	130	6	10.9	71.0	"
11	"	" "	130	6	63.7	20.0	"
12	Mercuribisthiosalicylic acid	" "	130	6	0.0	–	–
13	" "	" "	130	3	20.1	–	Thiosalicylic acid
14	" "	" "	130	6	30.2	–	" "
15	Ditolylmercury	Thiosalicylic acid	130	3	2.2	85.0	Toluene
16	Dibenzylmercury	" "	130	3	76.8	10.0	Dibenzyl
17	Dinaphthylmercury	" "	130	3	68.7	18.5	Naphthalene

NOTES: 1. The R_2Hg: thio acid ratio was 1:2 in all the tests, except in Test 10 (1:3 ratio) and Test 11 (1:10 ratio). 2. Alcohol was the solvent in all the tests, except: No. 8 (xylene) and No. 9 (no solvent used). 3. Reacting diphenylmercury with salicylic acid (1:2 ratio) for 3 hours at 130° yields phenylmercury salicylate, $C_6H_4(OH)COOHgC_6H_5$, quantitatively, no metallic mercury separating out.

When RHgHal is reacted with thiosalicylic acid, decomposition follows two lines, as in the case of R_2Hg, the sole difference being that Hg_2Hal_2 is formed instead of metallic mercury:

$$RHgHal + 2HSC_6H_4COOH \rightarrow Hg(SC_6H_4COOH)_2 + RH + HHal, \quad (7)$$

$$2RHgHal + 4HSC_6H_4COOH \rightarrow Hg_2Hal_2 + 2RH + 2HHal + 2(HOOCC_6H_4S)_2. \quad (8)$$

When RHgHal is reacted with thiophenol, the reaction is almost wholly analogous to that of diphenylmercury (Equation 3):

$$RHgHal + 2HSC_6H_5 \rightarrow Hg(SC_6H_5)_2 + RH + HHal, \quad (9)$$

$$RHgHal + 2HSC_6H_5 \rightarrow Hg + RH + HHal + (C_6H_5S)_2. \quad (10)$$

EXPERIMENTAL

All the experiments were performed by heating a mixture of the reagents in sealed ampoules immersed in thermostats whose temperatures were accurately controlled.

1. Diphenylmercury and thiosalicylic acid (130°, 3 hours). 0.5 gram of thiosalicylic acid was used with 0.5 g of diphenylmercury (1:2.2 ratio), plus 3 ml of alcohol. After the heating was over, benzene was found in the alcoholic solution, while 0.1004 g (35.44%) of metallic mercury was recovered from the precipitate, the

precipitate readily dissolving in a water-alcohol solution of alkali and settling out again when the solution was acidulated. Double reprecipitation and recrystallization from alcohol yielded 0.25 g of mercuribisthiosalicylic acid as white cubes with an m.p. of 250-251°. This compound was cleaved by prolonged boiling in an alcoholic solution of HCl, yielding $HgCl_2$ and thiosalicylic acid.

0.05 g substance: 1.97 ml 0.1 N NH_4CNS. Found %: Hg 39.42. $Hg(SC_6H_4COOH)_2$. Calculated %: Hg 39.60.

The alcoholic mother liquor yielded 0.05 g of the light-yellow crystals of diphenyldisulfidedicarboxylic acid, with an m.p. of 286° (the m.p. is given in the literature as 288°).

TABLE 2
Reaction of RHgHal with Thiosalicylic Acid

No.	RHgHal	t°	Time, hours	Per cent Hg_2Hal_2	Per cent $Hg(SC_6H_4COOH)_2$ produced	Other reaction products
1	C_6H_5HgCl	130°	3	–	64.0	HCl, C_6H_6
2		130	6	18.0	46.3	HCl, C_6H_6
3	C_6H_5HgBr	100	6	–	16.0	HBr, C_6H_6
4		130	3	7.0	60.0	HBr, C_6H_6
5		130	6	21.2	53.5	HBr, C_6H_6
6	$CH_3C_6H_4HgBr$	100	6	–	30.0	HBr, $C_6H_5CH_3$
7		130	3	4.8	56.0	HBr, $C_6H_5CH_3$
8		130	6	33.3	50.0	HBr, $C_6H_5CH_3$
9	$C_{10}H_7HgBr$	130	3	14.2	58.0	HBr, $C_{10}H_8$
10	$C_6H_{11}HgBr$	130	3	1.5	40.0	–
11	C_2H_5HgBr	130	3	1.0	34.0	–

NOTES: 1. The following quantities were used in all the tests: 0.001 mole of RHgHal; 0.002 mole of thiosalicylic acid; and 3 ml of alcohol. 2. Mercuribisthiosalicylic acid, $Hg(SC_6H_4COOH)_2$, with an m.p. of 250-251° and a mercury content of 39.35-39.55% (theoretical content = 39.60%), was produced in every test. 3. No reaction occurred when C_6H_5HgBr and C_2H_5HgBr were reacted with salicylic acid at 130°.

TABLE 3
Reaction of RHgHal with Thiophenol

No.	RHgBr	t°	Time, hours	% metallic Hg	% $Hg(SC_6H_4COOH)_2$ produced
1	C_6H_5HgBr	130°	3	28.6	70
2	$CH_3C_6H_4HgBr$	130	3	9.3	86
3		130	6	32.9	65
4	C_2H_5HgBr	130	6	24.7	72

NOTES: 1. 0.3 gram of RHgBr, 0.3 g of thiophenol, and 3 ml of alcohol used in all tests. 2. Mercury thiophenolate, $Hg(SC_6H_5)_2$, with an m.p. of 150-151° and a mercury content of 47.60-47.75% (theoretical content = 47.92%), was produced in every test, and diphenyl disulfide (0.1-0.12 g) was formed. 3. No reaction occurred when C_2H_5HgBr or C_6H_5HgBr was heated to 150° with phenol, cresol, nitrophenols, and resorcinol.

2. Phenylmercury chloride and thiosalicylic acid (130°, 6 hours). 0.65 g of thiosalicylic acid was used for 1.0 g of phenylmercury chloride (1:1.3), plus 5 ml of alcohol. HCl and benzene were found in the alcoholic solution after it had been heated. Hg_2Cl_2 (18%) and 0.75 g of mercuribisthiosalicylic acid, with an m.p. of 250°, were recovered from the precipitate.

0.052 g substance: 2.05 ml 0.1 N NH_4CNS. Found %: Hg 39.42. $Hg(SC_6H_4COOH)_2$. Calculated %: Hg 39.60.

3. Phenylmercury bromide and thiosalicylic acid (130°, 6 hours). 0.65 g of thiosalicylic acid was used for 1.0 g of phenylmercury bromide (1:1.5 ratio), plus 5 ml of alcohol. HBr, benzene, and Hg_2Br_2 (21.2%) were found in the reaction products. 0.75 gram of mercuribisthiosalicylic acid, with an m.p. of 250-251°, was recovered.

0.055 g substance: 2.16 ml 0.1 N NH_4CNS. Found %: Hg 39.27. $Hg(SC_6H_4COOH)_2$. Calculated %: Hg 39.60.

4. p-Tolylmercury bromide and thiosalicylic acid (130°, 6 hours). 0.62 g of thiosalicylic acid was used for 1.0 g of tolylmercury bromide (1:1.5 ratio), plus 5 ml of alcohol. HBr, toluene, and Hg_2Br_2 (33.37%) were found in the reaction products. 0.68 g of mercuribisthiosalicylic acid, with an m.p. of 250-252°, was recovered.

0.0482 g substance: 1.89 ml 0.1 N NH_4CNS. Found %: Hg 39.21. $Hg(SC_6H_4COOH)_2$. Calculated %: Hg 39.60.

5. Mercuric bromide and thiosalicylic acid. Mercuric bromide and thiosalicylic acid (1:2 ratio), dissolved in alcohol, yielded HBr and mercuribisthiosalicylic acid, at room temperature as well as when heated to 130°.

0.0491 g substance: 1.94 ml 0.1 N NH_4CNS. Found %: Hg 39.51. $Hg(SC_6H_4COOH)_2$. Calculated %: Hg 39.60.

6. Triphenylbismuth and thiosalicylic acid (100°, 3 hours). 1.05 grams of thiosalicylic acid was used for 1.0 g of triphenylbismuth (1:3 ratio), plus 6 ml of alcohol. Benzene was found in the alcoholic solution. The precipitate yielded 0.63 g of lustrous yellow crystals, which did not melt below 300° and were insoluble in organic solvents. These crystals dissolved at once in mineral acids, losing their color and yielding thiosalicylic acid and the respective $Bi^{\cdots}$ salts.

0.1114 g substance: 0.0892 g $BiPO_4$. Found %: Bi 55.41. $C_7H_5O_3SBi$. Calculated %: Bi 55.29.

A similar derivative of thiosalicylic acid and bismuth was formed at 130°.

7. Tetraphenyllead and thiosalicylic acid (130°, 3 hours). 0.96 gram of thiosalicylic acid was used for 0.78 g of tetraphenyllead (1:4 ratio), plus 6 ml of alcohol. Benzene was found in the alcoholic solution after heating was over. Repeated processing of the precipitate with solvents yielded 0.57 g of lustrous white lamellae, which did not fuse up to 315°, were insoluble in organic solvents, were slightly soluble in alkali solutions and were readily soluble in mineral acids.

0.0690 g substance: 0.0560 g $PbSO_4$. Found %: Pb 55.36. $C_7H_4O_3SPb$. Calculated %: Pb 55.20

8. Tetraphenyltin and thiosalicylic acid (130°, 6 hours). 1.38 g of thiosalicylic acid was used for 0.96 g of tetraphenyltin (1:4 ratio), plus 8 ml of alcohol. Benzene was found in the alcoholic solution after heating was over. The precipitate yielded 0.5 g of a lemon-yellow powder, which did not fuse up to 320°, was insoluble in organic solvents and readily soluble in mineral acids

0.092 g substance: 0.0480 g SnO_2. Found %: Sn 41.10. $C_7H_4O_3SSn$. Calculated %: Sn 41.47.

SUMMARY

1. When the aromatic compounds of mercury, lead, tin, and bismuth are reacted with thiosalicylic acid, they yield hydrocarbons and metallic derivatives of the thiosalicylic acid of the $Me^X(SC_6H_4COOH)_X$ type.

2. When organomercury compounds of the RHgHal type are reacted with thiosalicylic acid, they yield $Hg(SC_6H_4COOH)_2$, RH, HHal, and Hg_2Hal_2.

3. When organomercury compounds of the RHgHal type are reacted with thiophenol, they yield $Hg(SC_6H_5)_2$, RH, Hg and $(C_6H_5S)_2$.

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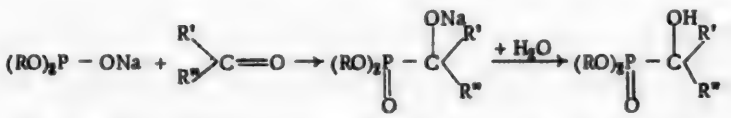
THE REACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

A NEW METHOD OF SYNTHESIZING ESTERS OF ALPHA HYDROXYALKYLPHOSPHINIC ACIDS

V. S. Abramov

Not much research has been done on the alpha hydroxyalkylphosphinic acids and their derivatives. The obvious reason is the difficulty of synthesizing and isolating them. The alpha hydroxyalkylphosphinic acids were first synthesized by Fossek [1] by reacting phosphorous trichloride with aldehydes or ketones and then treating the reaction products with water. Fossek secured several acids in this manner, but he was unable to produce the simplest hydroxymethylphosphinic acid. Then Marie [2] produced several alpha hydroxyalkylphosphinic acids by heating aldehydes and ketones with phosphorous acid or by reacting them with hypophosphorous acid and oxidizing the reaction products with bromine or mercuric chloride. Page [3] modified Fossek's method somewhat and secured a high yield of hydroxymethylphosphinic acid by reacting paraformaldehyde with phosphorus trichloride. Subsequently, A. E. Arbuzov and Kushkova [4] secured alpha hydroxymethylphosphinic acid by saponifying the ethyl ester of hydroxymethylphosphinic acid. Conant, McDonald, and Kinney synthesized various α-hydroxyphosphinic acids by reacting aldehydes and ketones with phosphorus trichloride, using various reagent ratios and temperatures, and then decomposing the reaction products with acetic acid. Conant and his associates likewise investigated the mechanism of this reaction. Fossek [1] isolated the diethyl ester of alpha hydroxyisoamylphosphinic acid as an oil by treating the product of the reaction between phosphorus trichloride and isovaleraldehyde with alcohol. Marie [2] secured the dimethyl ester of alpha hydroxybenzylphosphinic acid from the acid's silver salt and methyl iodide. A. E. Arbuzov and Kushkova [4] secured the diethyl ester of alpha hydroxymethylphosphinic acid by reacting sodium diethylphosphite with the ethyl ester of iodomethylphosphinic acid in aqueous alcohol. Kabachnik and Rossiiskaya [6] secured the dimethyl and diethyl esters of alpha hydroxybenzylphosphinic acid by reducing esters of alpha ketophosphinic acids with sodium amalgam in aqueous-alcoholic acetic acid.

The present paper describes a new method of preparing the diesters of alpha hydroxyalkylphosphinic acids. The method involves the direct action of aldehydes and ketones upon salts of dialkylphosphorus acids, as follows:

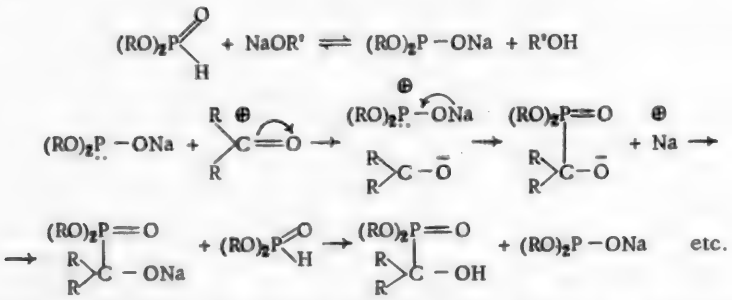


Diesters of alpha hydroxyalkylphosphinic acids were secured by treating the reaction products with acidulated water.

We are the first to have observed the addition of a sodium dialkylphosphite at the double bond in the carbonyl group of aldehydes and ketones. A. E. Arbuzov and Azanovskaya [7] had previously suggested a schema for the addition of sodium diethylphosphite at the carbonyl group of an ester of an alpha ketophosphinic acid by way of explaining the mechanism of the reaction of acetyl chloride with sodium diethylphosphite. They showed that an ester of alpha ketophosphinic acid reacts with sodium diethylphosphite. They did not isolate the reaction product, but they treated it with acetyl chloride. This resulted in the same product as that secured when acetyl chloride was reacted with sodium diethylphosphite, which, they thought, confirmed the schema they had advanced. They did not establish the structure of the end product, relying solely upon their determination of its molecular weight.

Esters of alkylphosphinic acids can be prepared in various ways [8]. The oldest and most commonly used

It must be supposed that aldehydes and ketones will also react with dialkylphosphorous acids if the acids have an enolic structure or are enolized during the reaction. B. A. Arbuzov and Pudovik [11] have shown that when sodium alcoholate is present, dialkylphosphorous acids add activated nitrile, carbonyl, and carboxyl groups at the ethylene bond. This method has been applied to reactions of aldehydes and ketones with dialkylphosphorous acids. The alcoholates of alkali metals, which enolize a dialkylphosphorous acid, make this reaction possible. In practice, a few drops of lithium or sodium methylate were used in our experiments. The reaction may be pictured as follows:



This chain reaction is rapid, considerable heat being evolved, and in most cases the yield of an ester of the alpha hydroxyalkylphosphinic acid is high. The completeness of the reaction depends upon the radicals in the carbonyl group: if the radicals reinforce the polarization of the molecule, the reaction is energetic, the yield being nearly quantitative, as in the case of benzoic aldehyde, whereas when the radicals diminish the polarization effect of the molecule, the reaction is moderated, and the yields are correspondingly low.

We have investigated the action of dimethylphosphorous, diethylphosphorous, and diisopropylphosphorous acids upon formaldehyde, acetaldehyde, butyraldehyde, benzaldehyde, acetone, acetophenone, cyclopentanone, and cyclohexanone. This resulted in production of the respective diesters of the alpha hydroxyalkylphosphinic acids, whose composition is:

R = CH_3, C_2H_5, and iso-C_3H_7; R' and R" are the radicals of the respective aldehydes and ketones.

EXPERIMENTAL

Action of aldehydes and ketones upon sodium dialkylphosphite. The sodium dialkylphosphite was prepared by the A. E. Arbuzov method [12], involving the action of a dialkylphosphorous acid upon metallic sodium in anhydrous ether. An aldehyde or a ketone was added to the resultant sodium dialkylphosphite, the reaction mass heating up until the ether boiled. The reaction products were processed with water acidulated with hydrochloric acid. The ether layer was separated and dried. After the ether had been driven off, the residue either crystallized or was distilled in vacuo.

Action of aldehydes and ketones on dialkylphosphorous acids. Equimolecular quantities of the aldehyde or ketone and the dialkylphosphorous acid. Some drops of lithium or sodium methylate were added to the mixture. The progress of the reaction was checked by the rise in the temperature of the reaction mixture as the alcoholate was added. The temperature rose 30 to 60°, as a rule; then heating to 100-125° was continued for a short time. The reaction products either crystallized upon cooling or were fractionated in vacuo.

The experimental findings are listed in the table.

SUMMARY

1. A new reaction has been found for the interaction of salts of dialkylphosphorous acids with aldehydes and ketones, resulting in the formation of esters of alpha hydroxyalkylphosphinic acids.

2. This reaction with dialkylphosphorous acids is easier and simpler when alcoholates are present.

3. This reaction holds both for aldehydes and ketones.

4. The new reaction makes it possible to synthesize a large number of various esters of alpha hydroxyalkylphosphinic acids.

5. The synthesized esters can be employed as the initial substances for further investigations.

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USING KETENE AS AN ACETYLATING AGENT

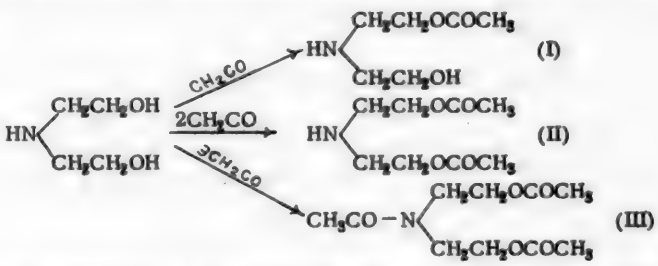
III. ACETATES OF DI- AND TRIETHANOLAMINES

A. A. Ponomarev and Yu. B. Isaev

The ethanolamines and their numerous derivatives are widely employed in various industries. In the past, however, the acetates of the ethanolamines have been known only as their derivatives [1, 2, 3], except for triethanolamine triacetate, which was synthesized by Ciusa and Sollazo, who used acetic anhydride and phosphoric acid [4].

We have reported [5] that high yields of the monoacetate and the diacetate are secured, depending on the conditions employed, when monethanolamine is reacted with ketene. Sodium acetate is the most effective catalyst in synthesizing monoethanolamine diacetate. The N-monoacetate is produced by reacting an aqueous solution of monoethanolamine with ketene; this method is based upon the difference in the reaction rates of ketene with the primary amino group and the hydroxyl group. The present paper sets forth the results of our experiments on the acetylation of di- and triethanolamines with ketene.

The acetylation of diethanolamine is rather complicated, due to the presence of chemically different reactive groups in that compound. The formation of the reaction products (I), (II), and (III) may be predicted:



In our experiments on the acetylation of diethanolamine with ketene we secured mixtures of acetates; we were unable to effect complete separation of the constituents of these mixtures by means of distillation.

Under the same conditions triethanolamine gave us 90 - 93% yields of the triacetate. This is apparently due to the fact that equivalent functional groups participated in the acetylation reaction in this instance, i.e., there is no fundamental difference between this process and the acetylation of such polyfunctional compounds as the glycols. It may be that the high yield of the triacetate (90%) when triethanolamine is acetylated without a catalyst is related to the catalytic action of the triethanolamine upon the products of its own acetylation.

EXPERIMENTAL [1)]

The ketene used in acetylation was produced in apparatus of our own design [6]. Acetylation was effected in small round-bottomed flasks fitted with outlet tubes, the ketene being bubbled (together with its accompanying gases) through a sample of the substance under acetylation. The reactors were immersed in water at 56 - 58° during acetylation.

Acetylation of diethanolamine. The diethanolamine had a b.p. of 141 - 144° (5 mm). 1. 20.00 grams

1) S. G. Tsypkina assisted in the experimental work (analyses).

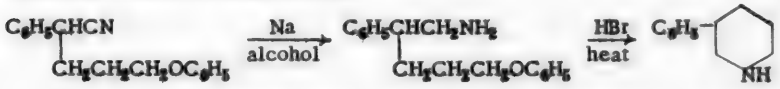
SYNTHESES EMPLOYING ACRYLONITRILE

XV. SYNTHESIS OF 3-PHENYL- AND 3,4-DIPHENYLPIPERIDINE

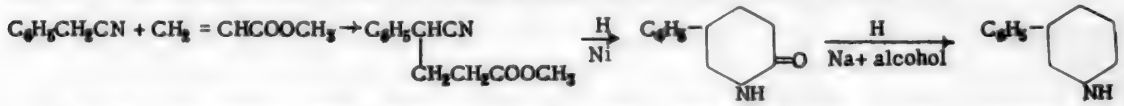
A. N. Kost and A. P. Terentyev

The β-arylpiperidines are cyclic analogs of the physiologically active bases of the phenamine type. That is why the physiological activity of 3-phenyl- [1] and 3,4-diphenylpiperidines [2] has been the subject of research, but the methods available for synthesizing these compounds were so complicated that it has been practically impossible to engage in any widespread product testing.

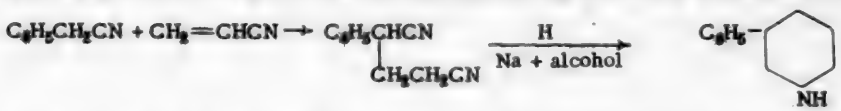
The synthesis of 3-phenylpiperidine by reducing the nitrile of α-phenyl-ω-phenoxyvaleric acid and then cyclizing it has been described [1]:



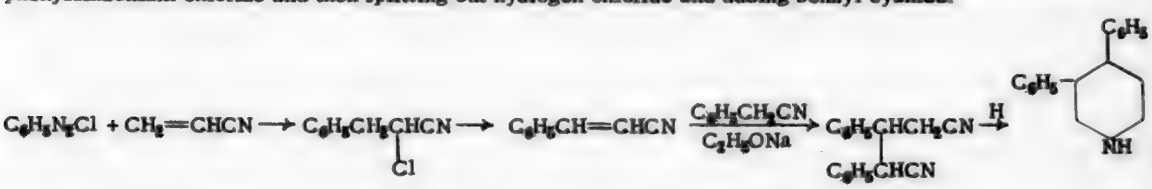
Koelsch [3] reacted methyl acrylate with benzyl cyanide and reduced the resultant methyl ester of γ-cyano-γ-phenylbutyric acid with skeletonized nickel (in alcohol at 200 atm and 150°), securing 5-phenylpiperidone-2, which was then converted into 3-phenylpiperidine by the action of sodium in alcohol.



We reacted benzyl cyanide with acrylonitrile and reduced the resultant α-phenylglutarodinitrile by the Vyshnegradsky method [4], i.e., with sodium in alcohol, immediately securing 59% of the theoretical yield of 3-phenylpiperidine.



Similarly, we secured yields up to 45% of the theoretical of 3,4-diphenylpiperidine by reducing the dinitrile of α,β-diphenylglutaric acid. We prepared the initial α,β-diphenylglutarodinitrile by reacting acrylonitrile with phenyldiazonium chloride and then splitting out hydrogen chloride and adding benzyl cyanide:



EXPERIMENTAL

Synthesizing α-phenylglutarodinitrile. 29.3 g (0.25 mole) of freshly distilled benzyl cyanide (b.p. 106-107° at 10 mm) and 13.7 g (0.3 mole) of acrylonitrile were placed in a 100-ml round-bottomed flask fitted with a reflux condenser. Then the mixture was shaken as 3 ml of sodium ethylate solution (1 g of sodium in 10 ml of absolute ethyl alcohol) was added. The mixture heated up spontaneously, the temperature rise being moderated by external water-cooling. After 20-30 minutes had elapsed, the violent reaction subsided, and the flask was heated for 30 minutes on a water bath (50-55°); after it had cooled, another 2 drops of sodium ethylate was added. The mixture was kept at room temperature for 4 hours, and then the flask's contents (a dark-olive liquid) were poured into 100 ml of 5% acetic acid. The organic layer was separated, washed with 10 ml of water, and dried with potash, the unreacted acrylonitrile being driven off, and the residue distilled in vacuo. This yielded 19.3-19.6 g (i.e., 45-46% of the theoretical) of α-phenylglutarodinitrile, with a b.p. of 184-187° at 9 mm. Refractionation yielded a b.p. of 181-183° at 8.5 mm; n_D^{25} 1.5237; d_4^{25} 1.0561; MR_D 49.31. $C_{11}H_{10}N_2$. Calculated 48.90.

Koelsch gives the b.p. at 198-200° at 18 mm. The yields when sodium methylate was used as a catalyst at 30-35° were: 36% in ether; 25% in an excess of phenylacetonitrile, and 0% in methanol or ethyl alcohol [5].

Synthesis of cinnamonitrile. 30 g of acetic acid and 100 ml of water were placed in a one-liter flask fitted with a mechanical stirrer, a thermometer, a reflux condenser, and a dropping funnel, and 70 ml of 40% potassium hydroxide was added. Then 15 g of cupric chloride, 250 ml of acetone, and 25 g (0.475 mole) of freshly distilled acrylonitrile were added. After this was done, a solution of phenyldiazonium chloride, prepared by diazotizing 48 g (0.5 mole) of aniline (35 g of sodium nitrite, 150 ml of water, and 10 ml of concentrated hydrochloric acid), was added drop by drop from a separatory funnel with vigorous stirring. Heat is liberated during the reaction. A piece of ice was therefore placed in the separatory funnel, and the reaction flask was chilled externally with ice, the temperature not being allowed to rise above 30°. After all the solution had been added, stirring was continued, the mixture being warmed to 50-55°, until no more nitrogen was evolved (about 2 hours). Then 200 ml of water was added, the oily layer was separated, the aqueous layer was extracted with ether three or four times and then dried with sodium sulfate, the ether, acetone, and acrylonitrile were driven off, and the residue was distilled in vacuo.

This yielded 23-26 g (i.e., 28-36% of the theoretical) of crude α-chloro-β-phenylpropiononitrile, containing cinnamonitrile as an impurity, since some hydrogen chloride was split out during distillation. B.p. 135-139° at 14 mm. Figures in the literature: b.p. 137-140° at 15 mm [5].

The cinnamonitrile was prepared by refluxing the crude α-chloro-β-phenylpropiononitrile (23 g) with five times its weight of dimethylaniline (115 g). Then the mixture was cooled, and 450 ml of 2N sulfuric acid was added with stirring and chilling. The oily layer was extracted with ether, washed with water, dried with potash, and distilled in vacuo. This yielded 14-15 g, or 77-83% of the theoretical, of cinnamonitrile, containing, apparently, a mixture of the cis and trans isomers. B.p. 113-115° at 15 mm; m.p. 20-22°; n_D^{25} 1.5846. Figures in the literature: b.p. 115-120° at 15 mm [5]; 128.8° at 12 mm [6].

Synthesis of α,β-diphenylglutarodinitrile. Six drops of sodium ethylate (1 g of sodium in 20 ml of absolute alcohol) was added to 11.7 g (0.1 mole) of freshly distilled benzyl cyanide. Then the flask was externally water-cooled and its contents stirred while 12.9 g of cinnamonitrile was added a drop at a time. If the mixture did not warm up spontaneously, 2 or 3 more drops of sodium ethylate were added. After addition was complete, the mixture was stirred for another hour at room temperature and for 1.5 hours at 40-50°, after which the reaction mass was poured into a mixture of ice and dilute acetic acid. The precipitate was suction-filtered and recrystallized from alcohol. This yielded 20.0-20.2 g, or 80-82% of the theoretical yield, of pure α,β-diphenylglutarodinitrile. M.p. 105°. The literature gives the m.p. as 101-103° [7].

Synthesis of 3-phenylpiperidine. 8.5 g (0.05 mole) of α-phenylglutarodinitrile was dissolved in 250 ml of n-butyl alcohol, and the solution was heated to 80-90° and then quickly poured over 19 g of metallic sodium (in a flask fitted with a slanting copper condenser). The mixture was heated on an oil bath (150-180°) until the sodium dissolved and then cooled, after which some water was added to decompose the alcohol, and the butyl alcohol and the amine were driven off with superheated steam (up to 180°) and collected in dilute hydrochloric acid. Then the butyl alcohol was separated, the alcoholic layer being washed three times with small portions of water, and the aqueous layer and the wash waters evaporated until crystallization set in. The resultant crude hydrochloride was deeply chilled and then decomposed with pulverized sodium hydroxide, 0.5 g of sodium sulfate being added to the alkali to prevent oxidation of the amine. The layered amine was extracted six or seven times with absolute ether (decantation), the combined extracts (some 150 ml) were dried with fused potassium hydroxide, the ether was driven off, and the residue was distilled in vacuo with a small dephlegmator. This yielded 4.75 g, or 59% of the theoretical yield, of 3-phenylpiperidine. B.p. 121-125° at 12 mm. Redistillation in vacuo in a current of anhydrous nitrogen yielded a b.p. of 125.5-126° at 12 mm; n_D^{20} 1.5256; n_D^{25} 1.5232; d_4^{25} 0.9592; MR_D 51.36. $C_{11}H_{15}N$. Calculated 51.04. The literature gives: b.p. 139-142° at 19 mm [3] and 255-256° at 740 mm [1].

The hydrochloride was secured by passing anhydrous hydrogen chloride through an ether solution of 3-phenylpiperidine. M.p. 143-143.5°. Koelsch [3] gives the m.p. as 143-144°. The picrate and the benzoyl derivatives are oils. The corresponding urethane, i.e., the ethyl ester of N-(β-phenylpiperidyl)-carboxylic acid, was prepared by the action of ethyl chloroformate, using the customary procedure [8]. B.p. 145-146° at 10 mm; n_D^{25} 1.5124.

4.805 mg substance: 0.253 ml N_2 (16°, 744 mm). Found %: N 6.09. $C_{14}H_{19}O_2N$. Calculated %: N 6.01.

Synthesis of 3,4-diphenylpiperidine. A solution of 14 g (0.057 mole) of α,β-diphenylglutarodinitrile in 220 ml of n-butyl alcohol was poured over 15 g of metallic sodium. The mixture was heated on an oil bath (180-200°) until the sodium had dissolved (about 45 minutes) and chilled, after which 100 ml of water was added and the mixture was steam-distilled for 4-5 hours, the distillate being collected in a receiver containing hydrochloric acid. The alcoholic layer was separated and washed with water, the aqueous solutions being combined and evaporated until crystallization set in and then decomposed with solid alkali. The amine produced was extracted with absolute ether, the extract being dried with fused potassium hydroxide, the ether driven off, and the residue distilled in vacuo. This yielded 3.0-6.1 g of 3,4-diphenylpiperidine, or 28-45% of the theoretical; the b.p. was 190° at 8 mm. The product crystallized after standing for a long time. M.p. 82-84°. The literature gives: b.p. 230-240° at 23 mm; m.p. 83-84° [3].

SUMMARY

1. Acrylonitrile has been used to synthesize the dinitriles of α-phenylglutaric and α,β-diphenylglutaric acids.

2. A Vyshnegradsky reduction of these dinitriles yielded 3-phenylpiperidine and 3,4-diphenylpiperidine, respectively, their respective yields being 59% and 45% of the theoretical.

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RESEARCHES ON BISULFITE COMPOUNDS

XV. THE STRUCTURE OF THE BISULFITE OF THE DYE ALIZARIN BLUE

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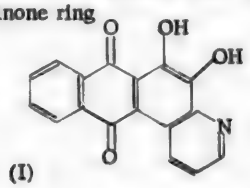
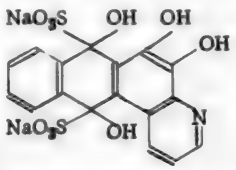
When the dye alizarin blue (I) is treated with sodium bisulfite, an additional product is formed, the dye being employed in dyeing in that form. Graebe and Brunk [1], who were the first to synthesize this compound, (like all later investigators) were unable to isolate it inthe pure state, owing to its low resistance to heat and to the action of alkalies. Only by analyzing the technical product and making a correction for the mineral salt content were they able to establish its empirical formula as $C_{17}H_9NO_4 + 2NaHSO_3$, i.e., as the product of the addition of two molecules of sodium bisulfite to one molecule of alizarin blue. They were unable to establish the structural formula of this compound, confining themselves to suggesting that the bisulfite was added to the nitrogen in the quinoline ring of the dye.

This viewpoint could not be maintained as time went on, since it was difficult to conceive how two molecules of bisulfite could be added to a single nitrogen atom; moreover the bond between the weakly basic nitrogen atom and the bisulfite ought to be hydrolyzed extremely easily by water and be broken down even more readily by the action of strong acids. On the other hand, the formation of the bisulfite compound involves the loss of the ability to form lakes; hence, the reaction affects the alizarin group that is needed for lake formation. That is why the structure of this compound is given in contemporary literature [2] as that of the addition product of sodium bisulfite and the carbonyl groups of the anthraquinone ring (II), without any additional research thereon having been done. When we examine this formula, we note that the carbonyl groups of the anthraquinone ring



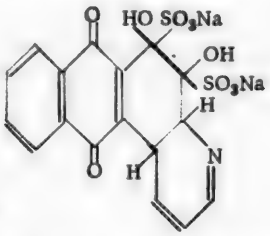
(I)



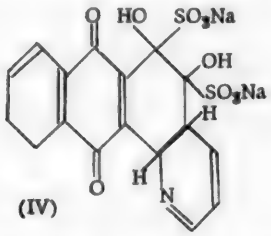
(II)

are not very reactive with the reagents that are typical for other quinones, not reacting, in particular, with bisulfite, as had been established by Graebe and Brunk long ago in the case of alizarin. In the anthraquinone series, condensation products with bisulfite are yielded only by alizarin blue and its isomer, alizarin green, and their derivatives [3], i.e., by compounds that contain a quinoline ring.

As has been shown by the researches of Vorozhtsov, Sr. and Kogan [4], the hydroxy derivatives of the quinoline series can react with bisulfite, yielding bisulfite compounds. We therefore assumed that the reaction with bisulfite ought to be similar in the anthraquinone dyes (of the alizarin blue and green type) as well, yielding their bisulfite compounds (III) in the case of alizarin blue and (IV) in the case of alizarin green:



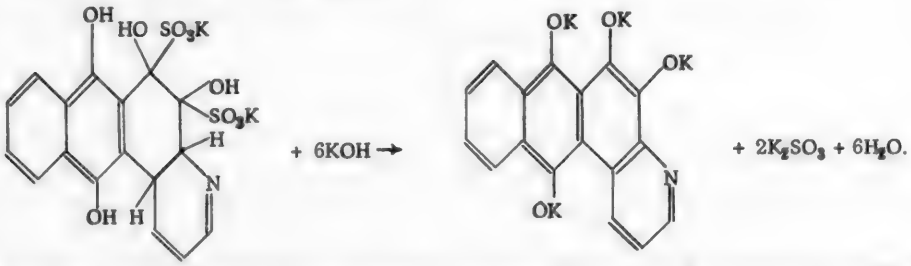
(III)



(IV)

It is not easy to establish the structure of these compounds, as the direct determination of the point at which the bisulfite groups are added is rendered quite difficult by their instability and the failure of their hydroxy groups to enter into acylation reactions (like other bisulfite compounds [5]). We tried to establish their structure by a different approach, proving that the products of the reaction between alizarin blue and bisulfite contain carbonyl groups by reducing them with zinc dust in the cold with acetic acid present. This treatment

of a solution of the pure potassium salt of the bisulfite compound we had produced resulted in a sharp change of the solution's color from reddish-brown to yellow. After the zinc dust had been filtered out, boiling the resultant yellow reduced solution readily split off its bisulfite groups, throwing down a brown precipitate of a leuco compound of alizarin blue, which is readily converted into the red vat typical of this dye by the addition of a caustic alkali in the cold with atmospheric oxygen excluded:



The reduced solution is readily reoxidized by atmospheric oxygen, while the vat dye produced is oxidized just as readily to the dye; this is why all this processing must be done with air excluded.

EXPERIMENTAL

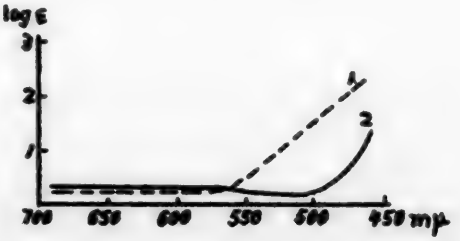
1. Potassium salt of the bisulfite compound of alizarin blue. 20 grams of a commercial 70% paste of the sodium salt of this bisulfite compound was dissolved in the cold in 150 ml of water. A small quantity of activated charcoal was added to the solution, which was then filtered, and 100 ml of a potassium carbonate solution, sp. gr. 1.18, was added. The crystalline precipitate of the potassium salt was filtered out and washed, first with 15 ml of the potassium carbonate solution referred to above, diluted to 50 ml with water, then with 100 ml of methanol, and finally with 50 ml of ether. The synthesized substance weighed 7.2 g after drying in air and then in a vacuum desiccator.

0.5897 g substance: 0.3045 g of pigment dye. 0.1968 g, 0.1367 g, 0.2222 g substance: 0.0610 g, 0.0419 g, 0.0685 g K_2SO_4. Found %: pigment dye 51.64; K 13.91, 13.75, 13.83. $C_{17}H_9NO_4 \cdot 2KHSO_3 \cdot 2H_2O$. Calculated %: pigment dye 51.31; K 13.78.

Under the microscope the potassium salt consists of light-brown prisms with tips cut off at a slant, grouped into hedgehogs; it is readily soluble in water, slightly soluble in methanol and ethyl alcohol, and insoluble in ether or most other organic solvents. It is readily hydrolyzed when heated with water above 60°; 20-30 minutes of boiling suffice for its complete hydrolysis, converting it into the thin violet needles of alizarin blue.

2. Reducing the bisulfite compound of alizarin blue. A 0.00002-molar solution of the potassium salt was prepared by dissolving 0.1135 g of the salt, together with 5 ml of a sodium bisulfite solution, sp. gr. 1.32, and 25 ml of glacial acetic acid, in 2000 ml of water. 5 grams of zinc dust was added to 1000 ml of the resulting solution, and the mixture was agitated briefly and then quickly filtered on a Buchner funnel. During this processing the initial reddish-brown color of the solution changed rapidly to bright-yellow, which is the color of the leuco compound of the bisulfite alizarin blue. The spectra of the solution before and after reduction were photographed with a Goldberg spectrodensometer: the absorption of the initial solution of the bisulfite compound begins at 560 mμ and continues into the ultraviolet region; the absorption of its leuco compounds starts at about 490 mμ.

When the reduced solution of the bisulfite compound was allowed to stand exposed to the air, it oxidized rapidly, turning reddish-brown again; treating it with solid sodium hydroxide with air excluded colors it the characteristic red of the vat dye of alizarin blue (this reaction was performed without any sodium bisulfite being added before reduction).



Absorption spectra: 1) leuco form of the bisulfite compound of alizarin blue; 2) bisulfite compound of alizarin blue.

SUMMARY

1. The potassium salt of the bisulfite compound of alizarin blue has been secured in the pure state and its conversion into the leuco form when reduced has been established.

2. The spectrum curves of the bisulfite compound and of its leuco form have been plotted, and formulas for their structure as products of the reaction of bisulfite with their hydroxy groups are put forward.

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RESEARCH ON SULFONATION

XXII. SYNTHESIS OF NAPHTHALENE TRISULFOCHLORIDES

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We have previously described the synthesis of 1,3,5-naphthalene trisulfochloride by the action of chlorosulfonic acid upon 1,5-naphthalene disulfochloride. The present paper describes the sulfonation of five other naphthalenedisulfochlorides by the same methods and some results of our exploration of this reaction.

As we know, the sulfonation of naphthalene or of the sulfo acids produced by the direct sulfonation of naphthalene yields three isomeric trisulfo acids. Since the information in the literature on the synthesis of 1,3,5-naphthalenetrisulfonic acid has been cited previously [1], we supply below only the information on the synthesis of the 1,3,6- and 1,3,7-trisulfo acids.

Armstrong and Wynne [2] synthesized the 1,3,6-trisulfo acid, identified as the trichloride with the m.p. 194°, by reacting naphthalene with chlorosulfonic acid. Friedlander [3] notes that almost nothing but the 1,3,6-trisulfo acid is produced when the 1,6- and 2,7-disulfo acids are sulfonated. The synthesis of the 1,3,7-trisulfo acid is described in a German patent [4]. The 2,6-disulfo acid was sulfonated on a water bath with oleum, containing 2.2 moles of the free anhydride per mole of the disulfo acid. Fierz-David [5] described two ways of synthesizing the 1,3,6-trisulfo acid. In the first method, naphthalene is first sulfonated by the monohydrate to the β-monosulfo acid at 165°, and then to the 1,6-disulfo acid with 60% oleum (3.4 moles of the anhydride per mole of naphthalene), at 50° to begin with and then at 165°. In the second method, the naphthalene is first sulfonated to the 2,7-disulfo acid with the monohydrate at 165°, and then with oleum (3.15 moles of SO_3 per mole of naphthalene) at 125-170°. Ufimtsev and Krivoshlykova [6] modified the first method described by Fierz-David somewhat, adding the oleum in two batches. After the first batch of oleum was added, sulfonation and rearrangement of the remainder of the disulfo acids took place at 155°, the second batch of oleum then being used for sulfonation. This raised the yield of the 1-amino-3,6,8-trisulfo acid (T acid) from 62 to 68%. A new method of producing the 1,3,6-acid has been developed at the Dorogomilovo plant [7], consisting of the following: the naphthalene was sulfonated to the 1,5-disulfo acid, after which rearrangement was effected at various temperatures, and exhaustive sulfonation was effected with oleum. The yield of the T acid in the nitro mass was 70%. Vorozhtsov and Chuksanova [8] sulfonated the 1,6-disulfo acid in the air and secured 80% of the theoretical yield of the 1,3,6-acid, the yield rising to 95% when the apparatus used was filled with nitrogen. Fierz-David and Richter [9] found that 87-92% of the 1,3,6-trisulfo acid and about 4% of other trisulfo acids were produced when 1,6- and 2,7-naphthalenedisulfo acids were sulfonated with an excess of oleum for 10 hours at 160°. These results indicate that at this temperature the di- or trisulfo acids are largely isomerized in fuming sulfuric acid, and that it is impossible to secure a pure trisulfo acid from the pure disulfo acids.

Thus, chlorosulfonic acid has never been used in sulfonation to produce naphthalene trisulfochlorides, and the trisulfo acids were never produced without traces of other isomers.

It is shown in the present paper that when the pure acid chlorides or salts of the 1,6- and 2,7-disulfo acids are processed with chlorosulfonic acid, pouring the reaction mixture out over ice yields the pure 1,3,6-trisulfochloride without any further refining. Similarly, the 2,6-disulfochloride yields the pure 1,3,7-trisulfochloride.

The results of our experiments on the chlorosulfonation of 1,6- and 2,7-naphthalene disulfochlorides set forth in Table 1 show that a highly pure 1,3,6-trichloride with a melting point that is at times as high as 197° is produced. (The highest melting point of 198° for the 1,3,6-trichloride was found by Ufimtsev and Krivoshlykova [6]). The reaction was not complete in Experiment 150, since the resultant trichloride was converted into a product with a m.p. of 195-195.5° when it was reprocessed with chlorosulfonic acid for 2 hours

TABLE 1

Synthesis of 1,3,6-Naphthalene Trisulfochloride From the 1,6- and 2,7-Dichlorides

Test No.	Used: Disulfochloride	Used: Moles of HSO_3Cl per mole of the chloride	Reaction temperature	Time, hours	Yield of the 1,3,6-trichloride, per cent of the theoretical	Melting point of the resultant trichloride
424	1,6-	4.7	125°	4	69.0	193-195°
145	1,6-	9.5	124	6	82.8	193-195
166	1,6-	10.2	149	1	82.7	194-195
110	1,6-	10.4	123	3	91.9	193.5-194
123	1,6-	14.3	125	3	85.5	194-195
125	1,6-	14.3	125	3	87.5	195-196
128	1,6-	20.1	125	3	94.4	194-195
394	2,7-	5	126	3	70.5	196-197
416	2,7-	4.9	125	6	72.8	193-195
149	2,7-	9.2	124	6	86.3	193.5-194
167	2,7-	10.2	149	1	85.2	195.5-196.5
148	2,7-	10.1	100	6	90.0	193.5-194
150	2,7-	14.4	100	2	91.9	188-191
46	2,7-	14.9	125	3	90.7	194-195
56	2,7-	14.5	125	3	92.5	194-195

at 100°. The yield of the trichloride ranges from 70 to 94% of the theoretical, depending on the amount of the excess and the quality of the chlorosulfonic acid. As has been reported previously [1], the chlorosulfonic acid, distilled in vacuo, contains a small amount of sulfuric acid, so that when it is sulfonated the yields of the trichloride are somewhat lower than the yields obtained when acid distilled at ordinary pressure is employed. What is more, using repeatedly distilled chlorosulfonic acid raises the yield of the trichloride.

TABLE 2

Chlorosulfonation of 2,6-, 1,7-, and 1,3-Naphthalene Disulfochlorides

Test No.	Used: Disulfochloride	Used: Moles of HSO_3Cl per mole of the chloride	Reaction temperature	Time, hours	Yield of trichlorides, per cent of the theoretical	Melting point of the resultant trichloride
112	2,6-	5.2	124°	6	69.1	163-165°
168	2,6-	10.2	149	1	77.5	163-164
108	2,6-	10.2	124	3	85.3	164-165
126	2,6-	14.6	125	3	91.5	164-165
44	2,6-	14.8	125	3	92.8	164-165
156	1,7-	14.5	100	4	85.4	126-139
160	1,7-	14.7	100	6	85.8	128-140
170	1,7-	20.4	100	8	90.5	130-142
169	1,7-	18.4	149	1	82.9	134-144
462	1,7-	32.1	146	1/2	86.1	135-144
45	1,7-	38.2	148	3	89.3	137-144
97	1,3-	16.8	150	3	97.1	115-128
463	1,3-	17.7	140-148	20 min.	81.0	120-125

The results of our experiments on the sulfonation of the 2,6-disulfochloride, given in Table 2, indicate that the 1,3,7-trisulfochloride secured is likewise highly pure (the highest melting point given in the literature for the 1,3,7-trichloride is 166°), its yield depending upon the amount of excess chlorosulfonic acid used and its quality.

Table 2 also gives the results of our experiments on the sulfonation of 1,7- and 1,3-naphthalene disulfochlorides. When the 1,7-dichloride is sulfonated, the sulfo group may be attached at the 3 or 5 position, yielding the 1,3,5- and 1,3,7-trisulfochlorides. As the 5 position is more reactive than the alpha position, the 1,3,5-isomer is produced with a low percentage of the 1,3,7-isomer, the resultant product having a melting point that is only a few degrees below that of the pure 1,3,5-trichloride. Our tests also indicated that less of the 1,3,7-isomer is produced at 146-148° than at 100°.

All three of the trisulfochlorides can be produced from the 1,3-disulfochloride, with the 1,3,5-isomer again predominating in the mixture apparently. The melting point of the product indicates, however, that appreciable percentages of the two other isomers are present.

TABLE 3

Synthesis of Naphthalene Trisulfochlorides From Sodium Salts of Disulfo Acids and Once-Distilled HSO_3Cl

Test No.	Used		Reaction temperature	Time, hours	Yield of trichlorides, per cent of the theoretical	Melting point of the resultant trichloride
	Salt of the disulfo acid isomer	Moles of HSO_3Cl per mole of chloride				
172	1,5-	25.3	149°	2	63.2	145-146°
171	1,6-	25.4	149	2	78.8	194-194.5
139	2,7-	29.4	124	6	61.3	195-196

Pure trisulfochlorides are produced when the sodium salts of the disulfo acids as well as the disulfochlorides are chlorosulfonated. The results of our experiments on the chlorosulfonation of the sodium salts of the 1,5-, 1,6-, and 1,7-disulfo acids, listed in Table 3, indicate that these trisulfochlorides are no less pure; their yields are much lower, however, than the yields secured when the disulfochlorides are sulfonated. The reason for the low yields of chlorides from the salts of sulfo acids have been set forth earlier [10].

We know that when sulfuric acid, oleum, and frequently even chlorosulfonic acid are used in sulfonation, by-products are obtained, the sulfomixture containing sulfones, resins, products of higher sulfonation, isomeric sulfo acids, and the unsulfonated initial product, in addition to the excess of the sulfonating agent. Hence the recovery and refining of the reaction product are often very troublesome operations. No sulfones, resins, and tetrasulfochloride are formed when the sodium salts of naphthalenedisulfonic acids and their acid chlorides are sulfonated with chlorosulfonic acid, nor is any unreacted disulfo derivative left.

We know that when 1,6- and 2,7-disulfo acids are sulfonated with oleum at 160°, the disulfo acids or the resultant trisulfo acid are isomerized appreciably [9]. No isomerization of the sulfo acids was found in our experiments. In most cases, however, we recovered far from all the disulfo acid as a chloride. It may be assumed that the free sulfo acid in the reaction mixture can be isomerized, the resulting isomers remaining in the solution after the reaction mixture has been poured over ice. To test this assumption, we ran experiments on the sulfonation of the 1,5-dichloride at 149°, the results being set forth in Table 4. When the reaction time was brief and the excess of the chlorosulfonic acid was small, we sometimes got a product containing a trace of the unreacted 1,5-dichloride, as indicated by its melting point. After the chloride had been precipitated, the aqueous solution, which contained sulfuric and hydrochloric acids, was evaporated on a water bath to constant weight in order to eliminate the latter acid, after which it was diluted with water and neutralized with barium carbonate, the barium sulfate being filtered out. The barium salts of the sulfo acids in the solution were converted into sodium salts with soda, the barium carbonate being filtered out, the filtrate evaporated to dryness, and the sodium salts converted into the acid chlorides.

The last columns in Table 4 give the percentages of the trichloride secured from the sulfo acid and its melting point. The experimental results show that the melting point of the trichloride produced initially is the same as that of the trichloride secured from the sulfo acids that remained in the filtrate when the reaction mixture was decomposed. This indicates that the sulfo acids are not isomerized when disulfo derivatives of naphthalene are chlorosulfonated at 150° for 6 hours. Moreover, if the reaction mass does contain a mixture of isomeric sulfo derivatives (or of di- and tri-derivatives), the composition of the mixture of isolated chlorides does not differ from that of the mixture of free sulfo acids dissolved in water when the reaction mass is decomposed.

It was noted earlier [1] that the rate of sulfonation with chlorosulfonic acid depends on how much of an excess of the acid is used. The more chlorosulfonic acid is employed per mole of the dichloride, the sooner the

TABLE 4

Conversion of the 1,5-Dichloride into the Trichloride and Analysis of the Filtrate After the Trichloride Had Been Precipitated by Pouring the Reaction Mixture Over Ice

Test No.	Moles of HSO_3Cl used per mole of the 1,5-dichloride	Reaction time, hours	Temperature	1,3,5-Trichloride Produced				Total yield, per cent of the theoretical
				Precipitated on Ice		From the filtrate via the sodium salt		
				Per cent of the theoretical	Melting Point	Per cent of the theoretical	Melting Point	
24	2.35	0.5	149°	59.5	127-134°	21.3	129-134°	80.8
18	4.70	0.5	148	67.4	140-141	21.9	140-141.5	89.3
22	7.82	0.5	148	81.9	146	8.4	145.5-146	90.3
27	2.36	4	149	40.1	144	54.5	144	94.6
23	7.82	6	149	77.8	144-144.5	14.1	144	91.9

formation of the trichloride is complete. The experimental results given in Table 5 show whether this depends upon the dilution of the chlorosulfonic acid by the sulfuric acid produced in the reaction or only upon the amount of chlorosulfonic acid active. The 1,5-dichloride was sulfonated with chlorosulfonic acid that had been distilled in vacuo, with and without the addition of 100% sulfuric acid. The results of six experiments, performed in pairs with all other conditions remaining the same, showed that the melting point of the product synthesized was practically the same in both cases, evidence of the identical proportions of the residual unsulfonated dichloride and the resultant trichloride. Hence, the rate of sulfonation depends upon the excess of chlorosulfonic acid used and not upon the percentage of sulfuric acid it contains (which ranges from 1 to 12% at most).

TABLE 5

Chlorosulfonation When the Chlorosulfonic Acid Contains Sulfuric Acid

Test No.	Moles of HSO_3Cl used per mole of the 1,5-dichloride	Per cent of H_2SO_4 in the HSO_3Cl	Reaction Temperature	Time, Minutes	Yield of the 1,3,5-trichloride, per cent of the theoretical	Melting point of the synthesized trichloride
175	7.19	1.0	100°	30	74.3	138-158°
176	7.24	11.6	100	30	61.5	135-159
91	7.54	1.5	125	20	76.7	136-140
90	7.42	10.6	125	20	63.6	135-139
86	7.54	2	125	60	77.4	145-145.5
87	7.49	10.9	125	60	61.8	145-145.5

We have shown earlier [1] that adding phosphoric anyhydride during the sulfonation of 1,5-naphthalene disulfochloride with chlorosulfonic acid raises the yield of the trichloride, due to the formation of pyrosulfuryl chloride ($S_2O_5Cl_2$) in the reaction mixture. The results of our experiments on sulfonation of the 1,5-dichloride with pyrosulfuryl chloride alone, prepared according to [11], and with a mixture of pyrosulfuryl chloride and chlorosulfonic acid, are given in Table 6. These experiments showed that pyrosulfuryl chloride by itself sulfonates much more slowly than does the chlorosulfonic acid. Experiment 83, for example, indicated that only a small portion of the dichloride was sulfonated in 3 hours at 125°, as shown by the melting point of the reaction product. Sulfonation for 12 hours did not yield a pure product, while prolonging the reaction time to 24 hours did not raise the melting point of the trichloride, but lowered it (Experiments 106 and 114). Hence, the action of pyrosulfuryl chloride also involves side reactions, their products contaminating the resultant trichloride. This is likewise shown by the results of Experiments 107 and 115.

Sulfonation with chlorosulfonic acid to which pyrosulfuryl chloride has been added yields much better results than sulfonation with chlorosulfonic acid or pyrosulfuryl chloride alone. The results of Experiment 94, for instance, indicated that 8.4 moles of chlorosulfonic acid plus 0.85 mole of pyrosulfuryl chloride produce a nearly quantitative yield of the trichloride, whereas the same yield requires no less than 25 moles of chlorosulfonic acid per mole of the dichloride when only the chlorosulfonic acid is used [1]. Similarly, 4.2 moles of chlorosulfonic acid plus 0.44 mole of pyrosulfuryl chloride give the same yield as secured with 10 moles of the chlorosulfonic acid alone.

TABLE 6

Chlorosulfonation with Pyrosulfuryl Chloride Alone and Mixed with HSO_3Cl.

Test No.	Moles used per mole of the 1,5-dichloride		Reaction temp.	Time, hours	Yield of the 1,3,5-trichloride, % of theoretical	M.p. of the synthesized trichloride
	HSO_3Cl	$S_2O_5Cl_2$				
83	–	5.06	125°	3	–	148-161°
106	–	4.94	125	12	90.7	141-142
114	–	5.20	125	24	95.4	137-139
107	–	2.54	125	24	92.3	141-142
115	–	2.56	125	48	88.9	135-139
85	4.29	0.45	125	3	86.1	142-143
106	4.21	0.44	125	6	85.6	145-146
94	8.43	0.86	125	6	98.7	145-146

All the experiments on the synthesis of the trichlorides were run in the same way as described in the previous report [1].

P. T. Pestova participated in this research.

SUMMARY

When the acid chlorides of 1,6- and 2,7-naphthalenedisulfonic acids or their sodium salts are sulfonated with chlorosulfonic acid, we get pure 1,3,6-naphthalene trisulfochloride after the mixture is decomposed on ice. Pure 1,3,7-naphthalene trisulfochloride is also secured from 2,6-naphthalene disulfochloride; the 1,3- and 1,7-dichlorides yield a mixture of trichlorides.

No isomerization of the naphthalenedi- or trisulfonic acids or of their chlorides occurs in chlorosulfonic acid at any temperature up to 150°, that is, up to their boiling point.

A given mixture of chlorides in chlorosulfonic acid containing sulfuric acid is partially converted into a mixture of the sulfo acids having the same composition as the mixture of chlorides.

The presence of sulfuric acid (up to 12%) in the chlorosulfonic acid has no effect upon its sulfonation rate.

Sulfonation with pyrosulfuryl chloride is much slower than sulfonation with chlorosulfonic acid.

The presence of about 0.1 mole of pyrosulfuryl chloride per mole of chlorosulfonic acid results in a considerable increase in the product yields during sulfonation.

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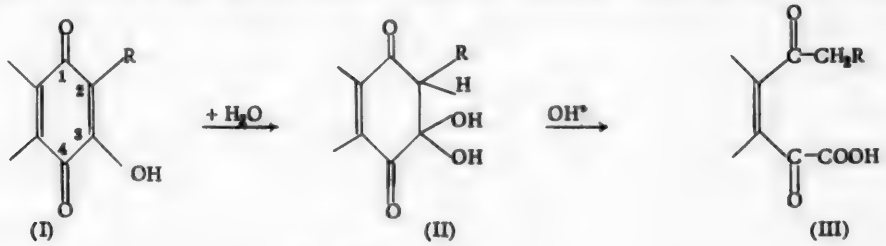
OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XXI. HYDROLYTIC CLEAVAGE OF 6-METHYL-3-HYDROXY-1,4-BENZOQUINONE*

L. A. Shchukina

During the past few years M.M.Shemyakin, together with the present author and other collaborators, has developed and laid the experimental underpinning for a theory of the oxidative-hydrolytic transformations of organic molecules [1-20], which makes possible a new approach to the cleavages of carbon bonds that occur when oxidative and hydrolyzing agents act together or consecutively.

In one of our preceding reports [19] it was shown, in connection with the relationship existing between the degree of oxidation of carbocyclic compounds and the ability of their ring groups to undergo hydrolytic cleavage, that hydroxyquinones of Type (I), which contain a hydrogen atom or an alkyl radical at the 2 position, ought to be cleaved readily, because of their structural peculiarities, when hydrolyzing agents are present, as follows:



(I) (II) (III)

R = H or Alk.

Up to the present time, however, the feasibility of this reaction has been established only for the respective naphthalene and phenanthrene hydroxyquinones, viz.: 3-hydroxy-1,4-naphthoquinone, 2-methyl-3-hydroxy-1,4-naphthoquinone, 2-hydroxy-1,4-phenanthrenequinone, and 3-hydroxy-1,4-phenanthrenequinone, which are readily cleaved hydrolytically in accordance with the foregoing schema [3,4,21]. As for the analogous hydroxyquinones of the benzene series, no research has yet been done on the conditions and nature of the hydrolytic cleavage of their ring groups. We were therefore interested in exploring this problem, using one of the simplest representatives of the hydroxybenzoquinones, in order to show that the reaction in question applies to all the Type (I) hydroxyquinones, no matter to what series they belong. Research on the hydroxybenzoquinones is also of interest from the biochemical standpoint, since M.M.Shemyakin believes that the phenylalanine–tyrosine interchange within the organism, involving the cleavage of their aromatic rings, probably occurs as follows: these amino acids are first oxidized to quinolylalanine and then to hydroxyquinolylalanine the ring grouping of which is then cleaved hydrolytically. Inasmuch as 6-methyl-3-hydroxy-1 4-benzoquinone (IV) is fairly close to quinolyl- and hydroxyquinolylalanine, among the simplest benzene hydroxyquinones, we chose this hydroxybenzoquinone as the first object of our investigation.

As was to have been expected on the basis of the theoretical considerations set forth previously [19], 6-methyl-3-hydroxy-1,4-benzoquinone (IV) proved that it could be first hydrated (with and without atmospheric oxygen present) and then cleaved hydrolytically in accordance with the equation below, it being found that the conditions required for this process are much milder than for the corresponding hydroxynaphtho- and hydroxyphenanthrenequinones: ** (see following page).

Hence, the hydrolytic cleavage in question is actually common to all Type (I) hydroxyquinones, no matter whether they belong to the benzene, naphthalene, or phenanthrene series.

Another significant fact is that 6-methyl-3-hydroxy-1,4-benzoquinone (IV) is hydrated more easily than the intermediate compound (V) is cleaved hydrolytically. This made it possible to divide the process into two stages,

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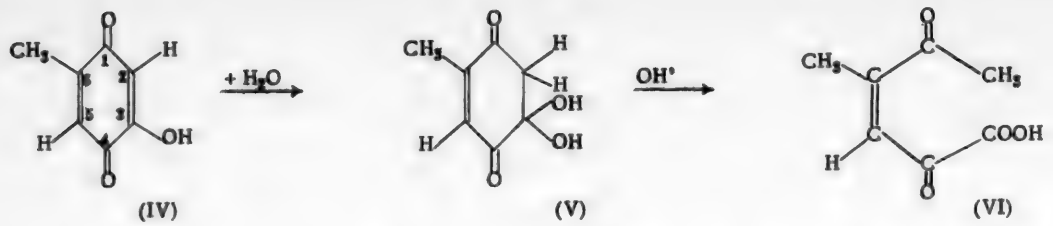
*) Report XIII on the hydrolytic cleavage of carbon bonds.

**) Compare the experimental findings set forth in the present report with those described in the articles [3, 14, 21].



(IV) (V) (VI)

isolating the hydrated hydroxyquinone (V), which proved to be a quite stable compound. The isolation of this substance serves as experimental proof of the mechanism of hydrolytic cleavage of Type (I) hydroxyquinones previously advanced by M.M.Shemyakin and the present author [1,3,14,19], which has been merely a hypothesis up to now. On the other hand, the isolation of the intermediate hydrated hydroxyquinone (V) enabled us to make a separate study of each of the stages involved in the conversion of the initial 6-methyl-3-hydroxy-1,4-benzoquinone (IV) into the final diketocarboxylic acid (VI). We found that the first stage – hydration – can be carried out by heating an aqueous solution of 6-methyl-3-hydroxy-1,4-benzoquinone, whose initial pH is 7, to 37° for 48 hours. The second stage – the hydrolytic cleavage of the hydrated hydroxyquinone (V) to the diketocarboxylic acid (VI) – takes place only when the solution pH exceeds 7, the process being quantitative when a 0.1 N aqueous solution of alkali is present, concluding within half an hour at 20°; when the solution pH is 9.17, the process requires 72 hours of heating to 37°. It is therefore beyond doubt that it is easier to hydrate the double bond in the 6-methyl-3-hydroxy-1,4-benzoquinone molecule than to hydrolyze the single carbon bond thereafter. This is apparently a universal phenomenon, as was stressed by M.M.Shemyakin and I.A.Redkin as far back as 1941 in their exposition of their theory of the hydrolytic cleavage of carbon bonds [22].

No difficulty is experienced in isolating the intermediate hydrated hydroxyquinone (V) when the conditions outlined above for the hydration of 6-methyl-3-hydroxy-1,4-benzoquinone (IV) are observed (see the experimental section of this paper). Proof of the structure of this compound required special study, however, since hydrated hydroxyquinones of this type have been wholly unknown hitherto.

In contrast to the bright-yellow initial hydroxyquinone (IV), the product of its hydration (V) we isolated is a white crystalline substance that fused with decomposition at 234°. The analytical data and the results of our determination of the molecular weight of this compound indicate an empirical formula of $C_7H_8O_4$, which is evidence that one molecule of water has been added to the molecule of the original hydroxyquinone. This water cannot be eliminated by recrystallizing the substance from organic solvents or by drying it in vacuo at 5 mm; the only way the elements of water can be removed is by using concentrated sulfuric acid or by subliming the substance in vacuo (280-300° at 5 mm), 6-methyl-3-hydroxy-1,4-benzoquinone (IV) being produced in both instances. These findings indicate that the compound we have isolated is not a crystal hydrate and that it possesses the carbon ring skeleton of the original hydroxyquinone.

These facts are not enough, however, to resolve the problem of the position at which the elements of water are added to the molecule of 6-methyl-3-hydroxy-1,4-benzoquinone (IV), as the latter can be hydrated either at the $>C=C<$ double bond or at the $>C=O$ double bond. Inasmuch as the hydration product would have to contain two hydroxyl groups in the former case and three in the latter, the solving of this problem may be reduced to a determination of the number of hydroxyl groups in the molecule of our synthesized compound. We found that this substance possesses only two active hydrogen atoms, while a diacetyl derivative, rather than a triacetyl one, is produced when it is acetylated with acetic anhydride in the presence of sulfuric acid. This demonstrates that when the hydroxyquinone (IV) is hydrated, the elements of water are added at one of the double bonds of the quinone ring rather than at the carbinol group.

There remains to consider the question of which of the ring's double bonds (the 2,3 or the 5,6 bond) undergoes hydration. As has been stated above, we secured a quantitative yield of nothing but a diketocarboxylic acid when we cleaved the hydrated hydroxyquinone hydrolytically. The only way in which that acid can be formed is by the hydroxyl group entering the quinone ring at the 3 position when the original hydroxyquinone is hydrated, with the hydrogen atom entering at the 2 position, inasmuch as any other order of addition of the elements of water would result in the formation of polycarbonyl compounds as the hydrolysis end products instead of the diketocarboxylic acid we recovered. There is, therefore, no doubt that the product of the hydration of 6-methyl-3-hydroxy-1,4-benzoquinone has the structure represented by Formula (V).

The diketocarboxylic acid produced in the hydrolytic cleavage of the compound (V) is not described in

the literature. It is a white crystalline substance that melts with decomposition at 258°; it crystallizes from water with 1,5 molecules of the solvent, after which it fuses at 203° with decomposition. The data of the analysis of the anhydrous acid and the results of a determination of the molecular weight of one of its derivatives (see the experimental section of this paper) indicate that this acid has the empirical formula of $C_7H_8O_4$. Hence, this acid is an isomer of the hydrated hydroxyquinone (V). The presence of a single carboxyl group in its molecule was established by titrating the acid directly with an alkali solution; we also secured the corresponding p-nitrobenzyl ester. The latter, as well as the acid itself, yields mono-p-nitrophenylhydrazones.

When the acid we had synthesized was heated with ammoniacal silver nitrate, a silver mirror was formed, due to the presence of the $-CO-COOH$ group in its molecule. Iodoform was produced by the action of an alkaline hypoiodite solution upon the acid; this is evidence of the presence of a $-CO-CH_3$ group, whence it follows that the acid in question is an acyclic compound. These findings indicated that the acid contains two active hydrogen atoms, one belonging to the carbonyl group, and the other to the $-CO-CH_3$ group.

Thus we have shown that all the three groups that were to be expected in the acid in question on the basis of its hypothetical structure are actually present in it. In the light of the conditions governing its formation and the structure of the initial compounds (IV) and (V), it is certain that this acid has the structure represented by Formula (VI).

EXPERIMENTAL *

Synthesis of 6-methyl-3-hydroxy-1,4-benzoquinone. We synthesized this quinone by the method described by Thiele and Winter [23]. This method consists of the following three stages: 1) acetylating toluquinone with acetic anhydride in the presence of sulfuric acid; 2) saponifying the resulting 2,4,5-triacetoxytoluene to 2,4,5-trihydroxytoluene with sulfuric acid in methanol; and 3) oxidizing the trihydroxytoluene to 6-methyl-3-hydroxy-1,4-benzoquinone (IV) with ferric chloride.

The first stage of this synthesis involved no difficulty, the yield of the 2,4,5-triacetoxytoluene, with a m.p. of 114-115° (from methanol) being 70%. But when we endeavored to reproduce the second and third stages, we either failed to obtain the end product (IV) entirely or else its yield was negligible. We were therefore obliged to modify the reaction conditions somewhat, enabling us to secure a 50% yield of the 6-methyl-3-hydroxy-1,4-benzoquinone, based on the 2,4,5-triacetoxytoluene. The modified procedure used to secure this quinone is set forth below.

120 grams of methanol, 4 g of concentrated sulfuric acid, and 100 g of 2,4,5-triacetoxytoluene were placed in a round-bottomed flask fitted with a reflux condenser. The resultant solution was boiled for 45 minutes, after which the reaction mass was cooled, 4.5 g of calcined soda was added to it, and 75-80 ml of the methanol was driven off. The residue was poured into 100 ml of a saturated aqueous solution of sodium sulfate and extracted 4 times with ethyl acetate. The ethyl acetate solution was dried with sodium sulfate, after which a large part of the solvent was driven off. The remaining liquid, which was still mobile, was transferred to a porcelain dish and evaporated to a thick brown syrup, which crystallized in part upon cooling. The resulting 50 g of 2,4,5-trihydroxytoluene can be oxidized to 6-methyl-3-hydroxy-1,4-benzoquinone (IV) without preliminary refining.

This was done by dissolving 50 g of the 2,4,5-trihydroxytoluene in 50 ml of a saturated solution of sodium chloride and dissolving 140 g of anhydrous ferric chloride in 280 ml of a 15% aqueous solution of sodium chloride, after which the first solution was poured into the second rapidly, with very vigorous stirring. The yellow hydroxyquinone (IV) was precipitated nearly instantaneously; it was rapidly filtered out on a Buchner funnel 1 to 2 minutes later. The precipitate was pressed out, washed with 20 ml of a saturated solution of sodium chloride, and immediately transferred, together with the filter, to a beaker containing 200 ml of ether. The aqueous layer was separated, the ether solution was dried with sodium sulfate, and the ether was driven off. The residue was recrystallized from benzene. This yielded 27 g of 6-methyl-3-hydroxy-1,4-benzoquinone, which fused at 142° with decomposition. The yield was 52%, based on the 2,4,5-triacetoxytoluene.

Hydration of 6-methyl-3-hydroxy-1,4-benzoquinone. 10 g of 6-methyl-3-hydroxy-1,4-benzoquinone was dissolved in 3 liters of distilled water at 37°, and the solution was kept in a thermostat at that temperature for 48 hours. After heating was over, 1 g of activated charcoal was added to the reaction solution, which contained a small amount of a tarry deposit, and the solution was allowed to cool to room temperature. Then the precipitate was filtered out, and the solution was evaporated to dryness in vacuo, at 40° and 10 mm.** The residue was washed twice in the flask with a small amount of ether, after which it was mixed with 10 ml of water, filtered out, and washed on the filter with 3 ml of water. The resultant white crystalline substance (5 g) was recrystallized from

*) We are indebted to E. A. Ignatyeva, who assisted in the analytical portion of the research

**) Violent frothing was observed during evaporation; it was eliminated by adding small quantities of octyl alcohol.

water containing activated charcoal. It was the hydrated hydroxyquinone (V), which crystallized from water in well-shaped rhombohedrons. After the substance had been dried in vacuo (100° and 5 mm) to constant weight, it fused at 234° with decomposition (first turning dark). The yield was 3.4 g, or 30%.

This compound is rather freely soluble in water, methanol, ethyl alcohol, acetone, and hot acetic acid, and sparingly soluble in ether.

Found %: C 53.97; H 5.08. M 158 (in dioxane). $C_7H_8O_4$. Calculated %: C 53.84; H 5.13; M 156.

The number of active hydrogen atoms (determined in pyridine by the Terentyev method) was 1.96 and 2.15.

Conversion of the hydrated hydroxyquinone (V) into the original hydroxyquinone (IV). a) 0.2 g of the hydrated hydroxyquinone (V) was dissolved in 3 ml of concentrated sulfuric acid. Three minutes later, the dark-red solution was poured into 150 ml of water and extracted 5 times with ether. The ether extract was extracted four times with a 10% solution of sodium bicarbonate, then acidulated with an aqueous solution of 20% sulfuric acid, and extracted several times with ether. The ether solution was dried with sodium sulfate, the ether driven off, and the residue washed with a few drops of ether. The resultant yellow crystalline substance fused at 140-142° and exhibited no depression of the mixed melting point with 6-methyl-3-hydroxy-1,4-benzoquinone. The yield was 25%.

b) 0.2 g of the hydrated hydroxyquinone (V) was sublimed in vacuo at 5 mm and 280-300°. The yellow crystalline sublimate was dissolved in ether, the 6-methyl-3-hydroxy-1,4-benzoquinone being recovered from the ether solution as described in Experiment (a). The quinone yield was 21%; m.p. 140-142°.

Acetylating the hydrated hydroxyquinone (V). 0.5 g of the hydrated hydroxyquinone (V) was added to 3 ml of acetic anhydride containing one drop of concentrated sulfuric acid; the substance did not dissolve completely. The next day the precipitate was filtered out and washed with alcohol. The resultant diacetyl derivative did not fuse when heated to 330°. Weight: 0.65 g; yield: 85%. This compound is sparingly soluble in alcohol, acetone, dioxane, nitrobenzene, and other organic solvents. It can be recrystallized from acetic anhydride, from which it settles out as rhombic crystals.

Found %: C 55.14; H 5.20. $C_{11}H_{12}O_6$. Calculated %: C 55.00; H 5.00.

The number of acetyl groups in the synthesized compounds was determined as follows. A sample of the substance (about 0.15 g) was placed in 3 ml of concentrated sulfuric acid. Two or three minutes later 25 ml of water was added to the dark-red solution, and the resulting acetic acid was driven off with steam; its percentage in the distillate was determined by titration with a 0.1 N alkali solution. The number of acetyl groups was found to be 2.03 and 2.12 by this method.

Hydrolytic cleavage of the hydrated hydroxyquinone (V). a) Cleavage with a 0.1 N alkali solution. 1.0 gram of the hydrated hydroxyquinone (V) was dissolved in a quantity of 130 ml of aqueous sodium hydroxide, and the colorless solution was allowed to stand for 30 minutes at 20°. Then 20 ml of 1 N sulfuric acid and 15 g of sodium sulfate were added, and the solution was evaporated to dryness in vacuo at 40° and 5 mm.* The dry residue was extracted with ether in a Soxhlet apparatus for 24 hours. Then the ether solution was evaporated to about 5 ml volume and the precipitated diketocarboxylic acid (VI) was filtered out. Decomp. temperature 258°. Yield: 0.1 g, or 100%.

Similar results were secured when this experiment was carried out in nitrogen.

The substance was recrystallized from 2 ml of water, from which it settled out as elongated white lamellae that contained 1.5 molecules of crystallization water. The crystal hydrate fused at 201-203° with decomposition after it had been air-dried.

Found %: C 45.67; H 6.12; M 184 (titration with 0.1 N alkali). $C_7H_8O_4 \cdot 1.5\ H_2O$.
Calculated %: C 45.90; H 6.01; M 183.

The crystallization water was eliminated by drying a sample of the substance in vacuo at 110° and 5 mm to constant weight. The decomposition temperature of the anhydrous acid was 258°.

Found %: H_2O 14.58. $C_7H_8O_4 \cdot 1.5\ H_2O$. Calculated %: H_2O 14.67.

Results of analysis of the anhydrous acid: Found %: C 53.86; H 5.12; M 158 (titration with 0.1 N alkali). $C_7H_8O_4$. Calculated %: C 53.84; H 5.13; M 156.

Number of active hydrogen atoms (determined in pyridine by the Terentyev method): 1.88.

* In this and other instances the sodium sulfate has to be added to effect more complete and satisfactory extraction of the dry residue from the flask after the water has been driven off in vacuo.

Both the aqueous and the anhydrous diketocarboxylic acid (VI) are freely soluble in water, methanol, ethyl alcohol, glacial acetic acid, and dioxane. When treated with ferric chloride it turns an intense brown; it does not decolorize bromine water. It forms a silver mirror only when heated with ammoniacal silver nitrate.

b) Cleavage in a buffer solution at pH 9.17. 1 g of the hydrated hydroxyquinone (V) was dissolved in 200 ml of aqueous disodium phosphate (pH 9.17; buffer capacity 0.1 mole), and the resultant solution was left in a thermostat for 72 hours at 37°. After the reaction was over, the solution was acidulated with 20% sulfuric acid until the pH = 1, after which the phosphoric acid was precipitated with calcium carbonate. The precipitate was filtered out and thoroughly washed with water, the filtrate being acidulated with sulfuric acid until its reaction with Congo red was acid and then evaporated to dryness in vacuo at 40° and 10 mm without filtering out the precipitated calcium sulfate. The dry residue was extracted with ether in a Soxhlet apparatus for 24 hours. Driving off the ether left an oily substance, containing phosphoric acid, which was dissolved in 50 ml of water, after which the phosphoric acid was reprecipitated with calcium carbonate. The precipitate was filtered out and washed with water, the filtrate acidulated with sulfuric acid until its reaction with Congo red was acid, 15 g of sodium sulfate added to the filtrate, and the solution evaporated to dryness in vacuo. The dry residue was extracted with ether for 24 hours in a Soxhlet apparatus. Driving off the ether yielded 0.8 g of an oily substance, to which 10 ml of benzene was added. The latter was evaporated to a total volume of 1-2 ml, 5 ml of ether being added to the residue and the precipitate being filtered out. Recrystallization from water yielded 0.3 g of the crystal hydrate of the diketocarboxylic acid (VI), which fused at 201-203° with decomposition.

Preparation of the p-nitrophenylhydrazone of the diketocarboxylic acid (VI). A solution of 0.65 g of p-nitrophenylhydrazine in 5 ml of 50% alcohol was added to a solution of 0.3 g of the acid in 5 ml of 50% alcohol. Two days later the reaction mixture was poured into 50 ml of water, and the resulting precipitate was filtered out. Recrystallization from 7 ml of 30% acetic acid yielded 0.2 g of a substance with a decomp. temp. of 290-292°.

Found %: C 53.35; H 4.73. $C_{13}H_{13}O_5N_3$. Calculated %: C 53.61; H 4.47.

Preparation of the p-nitrobenzyl ester of the diketocarboxylic acid (VI). 0.7 g of the acid was dissolved in 30 ml of water and accurately neutralized with a 0.1 N alkali solution, the resulting solution of the sodium salt being evaporated to a total volume of 5 ml; 1.1 g of p-nitrobenzyl bromide was heated in 10 ml of alcohol until it dissolved, and the aqueous solution of the sodium salt of the diketocarboxylic acid (VI) was added to the hot alcoholic solution. The mixture was boiled for 1 hour, a precipitate beginning to settle out after 40-45 minutes had elapsed. After the reaction mass had cooled, the precipitate was filtered out. Weight: 0.8 g. The resultant ester was recrystallized from 80% acetic acid, from which it settled out as elongated rhombohedra; m.p. 189°.

Found %: C 57.92; H 4.62. $C_{14}H_{13}O_6N$. Calculated %: C 57.73; H 4.46.

Preparation of the p-nitrophenylhydrazone of the p-nitrobenzyl ester of the diketocarboxylic acid (VI). 0.15 g of the p-nitrobenzyl ester described above was dissolved at 80° in 15 ml of glacial acetic acid; the solution was cooled to 25°, and 0.25 g of p-nitrophenylhydrazine dissolved in 10 ml of glacial acetic acid was added. Twelve hours later the reaction mixture was poured into 100 ml of water, the resulting precipitate being filtered out and washed with water. Weight: 0.25 g. The substance was recrystallized from 15 ml of glacial acetic acid and then dissolved in 3 ml of nitrobenzene heated to 80°; the resultant solution was cooled, and 10 ml of benzene was added. The resultant precipitate was filtered out 30 minutes later; it weighed 0.1 g and had a m.p. of 216-218°.

Found %: C 56.59; H 4.13; M 412 (in nitrobenzene). $C_{20}H_{18}O_7N_4$. Calculated %: C 56.34; H 4.22; M 426.

Determination of the $-CO-CH_3$ group in the molecule of the diketocarboxylic acid (VI). 0.3 g of the acid was dissolved in 10 ml of water, 1.9 g of iodine dissolved in 10 ml of a 20% aqueous solution of potassium iodide was added, and 10 ml of a 10% sodium hydroxide solution was gradually added to the resulting mixture. The solution was decolorized and iodoform gradually settled out. One hour later the latter was extracted repeatedly with ether, the ether solution being dried with sodium sulfate and the ether driven off. This yielded 0.06 g (10%) of iodoform, with a m.p. of 119°.

SUMMARY

The required conditions and the nature of the hydrolytic cleavage of 6-methyl-3-hydroxy-1,4-benzoquinone have been investigated. It has been shown that this process involves two stages: at first, the initial quinone is hydrated, and only thereafter is the ring grouping of the intermediate hydration product cleaved hydrolytically. The structure of this intermediate compound and of the final diketocarboxylic acid has been established.

Comparison of the results of these researches with the data published earlier indicates that hydrolytic ring cleavage is characteristic of all the hydroxy-1,4-quinones of benzene, naphthalene, and phenanthrene that contain a hydrogen atom or an alkyl radical at the 2 position and a hydroxyl group at the 3 position.

The mechanism of this reaction has been established experimentally.

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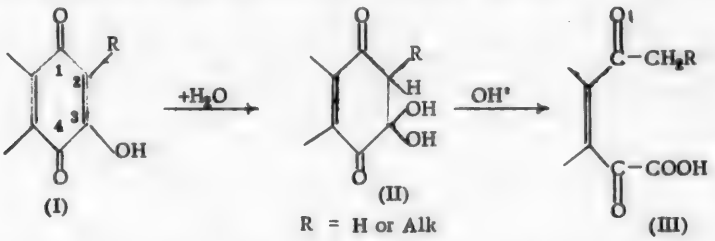
OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XXII. HYDROLYTIC AND OXIDATIVE TRANSFORMATIONS OF 1-BENZENEAZO-3,4-DIHYDROXYNAPHTHALENE[*]

O.M.Shemyakina, B.M.Bogoslovsky, and M.M Shemyakin

In several previous reports [1-4] it has been shown that the ring groups of molecules of Type (I) hydroxyquinones can be hydrated and then cleaved hydrolytically as follows:

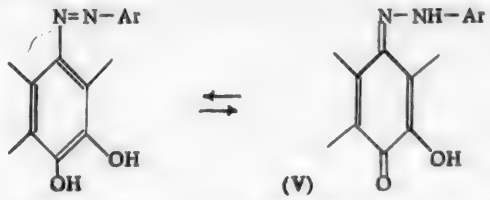


(I) (II) (III)

R = H or Alk

This reaction is easily carried out in the hydroxyquinones of the benzene, naphthalene, and phenanthrene series that contain a hydrogen atom or an alkyl radical at the 2 position, so that a tendency to such transformations may now be regarded as a characteristic feature of this group of hydroxyquinones.

It was highly probable that similar ring cleavage would take place in some hydroxyazo dyes, such as those of Type (IV), which may also exists in the tautomeric form (V) as we know:



(IV) (V)

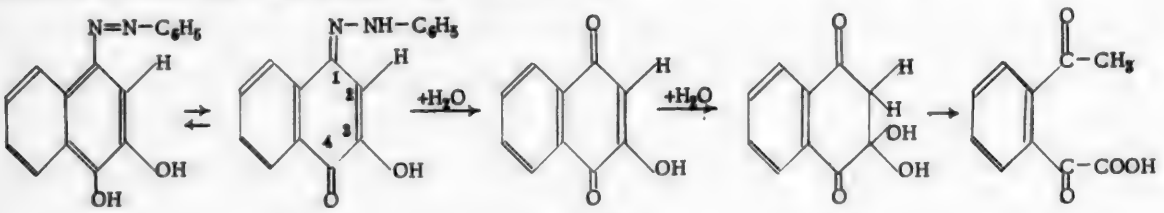
Compounds of the latter type may be regarded as arylhydrazones of the respective hydroxyquinones, and it is that very circumstance that led us to suppose that hydroxyazo dyes of Type (IV) would behave like the Type (I) hydroxyquinones in the presence of hydrolyzing agents.

In order to make an experimental study of this problem we chose as our first research object 1-benzeneazo-3,4-dihydroxynaphthalene (VI), which ought to undergo hydrolytic cleavage very readily, for the following reasons, as we saw it. Because of its structure this hydroxyazo dye can exist in aqueous solution in the tautomeric form (VII), the phenylhydrazone of 3-hydroxy-1,4-naphthoquinone (especially at values of pH in excess of 7). The 3-hydroxy-1,4-naphthoquinone itself, as has been shown previously [2], is readily cleaved to o-acetylphenylglyoxylic acid in accordance with the general reaction set forth above, (I) → (II) → (III), when it is boiled in an aqueous solution (pH = 7.3-9.5). We therefore thought that the tautomeric form (VII) of the initial hydroxyazo dye ought to be just as readily cleaved between the 2 and 3 carbon atoms, either before or after the phenylhydrazine group at the 1 position was split off.

An experimental study of the conditions and nature of the hydrolytic cleavage of the hydroxyazo dye (VI) we had chosen showed that this assumption was correct. This hydroxyazo dye begins to undergo a slow change when an aqueous solution that has an initial pH of 7 is boiled, provided atmospheric oxygen is excluded (nitrogen atmosphere). These changes occur very rapidly when the solution pH is 9, being fully

[1] Communication XIV on the hydrolytic cleavage of carbon bonds.

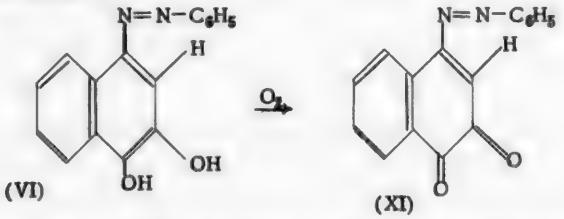
completed within 15 hours of boiling when that is so. We found that it is the quinoid form (VII) of the azo dye rather than the benzoid form (VI) that is cleaved hydrolytically, the (VII) form splitting off the phenylhydrazine group and being converted into 3-hydroxy-1,4-naphthoquinone (VIII), secured in yields as high as 50%, which then undergoes more far-reaching changes, being partially cleaved to o-acetylphenylglyoxylic acid (X); we isolated a small amount of this latter acid as the corresponding semicarbazone.



(VI) (VII) (VIII) (IX) (X)

Thus, the phenylazo group can be split out of the 1-benzeneazo-3,4-dihydroxynaphthalene molecule (VI) and one of the naphthalene rings can then be cleaved by the action of hydrolyzing agents alone, the required conditions being fairly mild.

It should be stressed that the hydroxyazo dye (VI) undergoes altogether different changes in aqueous or aqueous–alcoholic alkali solutions when atmospheric oxygen is present, being very readily converted into 1-benzeneazo-3,4-naphthoquinone (XI); in this latter case, it is not the quinoid form (VII) but the benzoid form (VI) of the initial hydroxyazo dye that undergoes oxidation.



(VI) (XI)

This process, first described by Zincke and Wiegand [5], has also been explored by us. We have found that oxidation of the hydroxyazo dye (VI) by oxygen in an aqueous–alcoholic alkali solution is completed within 2-2.5 hours at 5-10°, the yield of 1-benzeneazo-3,4-naphthoquinone (XI) being 65-70% under these conditions.* The ring of this azoquinone is unstable; heating an aqueous–alcoholic solution of the azoquinone to about 180° in nitrogen results in cleaving its molecule all the way to phthalic acid.

In conclusion, we might add that all hydroxyazo dyes whose structure resembles that of the 1-benzeneazo-3,4-dihydroxynaphthalene (VI) we have investigated ought to manifest instability when acted upon by oxidants and hydrolyzing agents.

EXPERIMENTAL

1. Hydrolytic cleavage of 1-benzeneazo-3,4-dihydroxynaphthalene. The experiment was performed in apparatus consisting of two 3-liter round-bottomed flasks. The first flask (A) was fitted with a reflux condenser and two tubes extending to the bottom of the flask. The other flask (B) was fitted with a reflux condenser, a dropping funnel, and one tube extending to the bottom of the flask. The two flasks were connected via a three-way stopcock, to which there were attached: one of the tubes in the flask (A), the upper end of the condenser fitted to flask (A), and the tube in flask (B). Nitrogen was supplied to the system through the other tube in flask (A), the nitrogen being purified by first passing it through an alkaline solution of pyrogallol and conc.sulfuric acid. The nitrogen had to pass through a tube filled with copper and heated to 400-450° to get rid of the last traces of oxygen. The system terminated in two Tishchenko bottles filled with an alkaline solution of pyrogallol, which were connected to the upper end of the condenser on tube (B).

3 g of 1-benzeneazo-3,4-dihydroxynaphthalene [5] was placed in flask (B), and 2 liters of a phosphate buffer solution (pH 9.17; buffer capacity 0.1 mole) in flask (A). The airtightness of the system was checked, and then we began to drive the air out of the system by nitrogen, the three-way stopcock being turned so as to connect the upper end of the condenser on flask (A) to the tube that reached to the bottom of flask (B).

* Zincke and Wiegand give 250° as the decomposition temperature of this azoquinone, whereas it actually fuses with decomposition at 205-207°.

At the same time the phosphate buffer solution in flask (A) was heated until it boiled. Two hours after the solution had started to boil, the three-way stopcock was turned so as to cover up the opening leading to the condenser of flask(A), and the air was driven out of the flask (A) tube by the buffer solution, without stopping the flow of nitrogen, the buffer solution rising up to the three-way stopcock. The three-way stopcock was then turned to its initial position and nitrogen was passed through for another 0.5 hour. Then the heating of flask (A) was stopped, the buffer solution was cooled, and the three-way stopcock was turned so as to connect the tube in flask (A) to the tube in flask (B), after which the buffer solution was transferred to flask (B), which contained the sample of the substance.

The resultant mixture was boiled in a current of nitrogen for 15 hours. After heating was complete, the reaction mixture was cooled, the solution pH was brought to 6-6.5 by adding 25% sulfuric acid, and the solution was then evaporated in vacuo in a current of nitrogen until its volume totaled some 200 ml. When it had cooled, the dark-brown precipitate was filtered out, and the brown-red filtrate was acidulated with 60% sulfuric acid. This threw down 0.78 g of a yellow precipitate, which had a m.p. of 190-191° after double recrystallization from methanol and exhibited no depression of the mixed melting point with 3-hydroxy-1,4-naphthoquinone.

The acid aqueous filtrate was extracted five times with ether, the ether extract was washed with water, boiled with activated charcoal, and dried with sodium sulfate, and the ether was driven off. This left 0.2 g of 3-hydroxy-1,4-naphthoquinone, which was washed with small portions of ether and ethyl alcohol and then recrystallized from methanol. M.p. 190-191°. The total yield of the 3-hydroxy-1,4-naphthoquinone was 49.5%.

The aqueous reaction solution left after the hydroxyquinone had been extracted with ether was evaporated in vacuo to a volume of 30-40 ml, the mineral salts being filtered out and the filtrate extracted with ether. The ether extract was boiled with activated charcoal, the ether driven off, and the yellow oily residue was dissolved in 2 ml of ethyl alcohol, after which a solution of 0.1 g of semicarbazide hydrochloride and 0.14 g of sodium acetate in 1 ml of water was added. A few days later 0.02 g of a precipitate that had a m.p. of 154-156° with decomposition settled out of the solution. After crystallization from water containing activated charcoal the substance had a m.p. of 158-160° with decomposition and exhibited no depression of the decomposition temperature when mixed with the semicarbazone of o-acetylphenylglyoxylic acid [2].

2. Oxidizing 1-benzeneazo-3,4-dihydroxynaphthalene. 1 gram of 1-benzeneazo-3,4-dihydroxynaphthalene was mixed with 25 ml of alcohol, and then a solution of 2 g of sodium hydroxide in 10 ml of water was added. Oxygen was passed through the resultant dark-blue solution, chilled to 5-10°, for 2-2.5 hours until the solution turned brown.*

Within 30-45 minutes a light-yellow precipitate began to settle out of the solution, its amount gradually increasing. When the reaction was over, the precipitate was filtered out, thoroughly mixed with 10-15 ml of water, refiltered, repeatedly washed on the filter with water. Weight: 0.70 g; 70% yield.

The synthesized 1-benzeneazo-3,4-naphthoquinone was purified by extracting it with ether in a device used for hot extraction. Light-yellow crystals that fused at 205-207° with decomposition settled out of the ether solution.

Found %: C 73.34; H 4.12. $C_{16}H_{10}O_2N_2$. Calculated %: C 73.28; H 3.84.

3. Cleaving 1-benzeneazo-3,4-naphthoquinone. 1 g of 1-benzeneazo-3,4-naphthoquinone was heated for 6 hours to 200° (bath temperature) with 30 ml of 20% aqueous alcohol in an autoclave (from which the air had previously been expelled by nitrogen). When the reaction was over, the black precipitate was filtered out, the filtrate being alkalinized and repeatedly extracted with ether. Then the aqueous-alkaline solution was acidulated with hydrochloric acid and evaporated to dryness. The residue was extracted with ether in a Soxhlet apparatus, the resulting ether solution boiled with activated charcoal and dried with

* Oxidation may also be effected with atmospheric oxygen, but then the reaction is slower.

sodium sulfate, and the ether driven off. The residual crystalline precipitate was washed with a few drops of ether and recrystallized from water. The substance fused with decomposition at 195-200° and exhibited no depression of the decomposition temperature when mixed with phthalic acid; it was converted to phthalic anhydride (m.p. 130-131°) by heating it above the decomposition temperature.

SUMMARY

It has been shown that 1-benzenazo-3,4-dihydroxynaphthalene is changed very readily when acted upon by oxidants or hydrolyzing agents. This hydroxyazo dye is readily oxidized in an aqueous-alcoholic alkaline solution to 1-benzeneazo-3,4-naphthoquinone by atmospheric oxygen at 5-10°, while in the absence of atmospheric oxygen it undergoes profound hydrolytic transformations when an aqueous solution with a pH of 9 is boiled. In the latter case, the 1-benzeneazo-3,4-dihydroxynaphthalene is first converted into the tautomeric quinoid form (the phenylhydrazone of 3-hydroxy-1,4-naphthoquinone), which splits off the phenylhydrazine group to yield 3-hydroxy-1,4-naphthoquinone, which is then partially cleaved to o-acetylphenylglyoxylic acid.

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OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

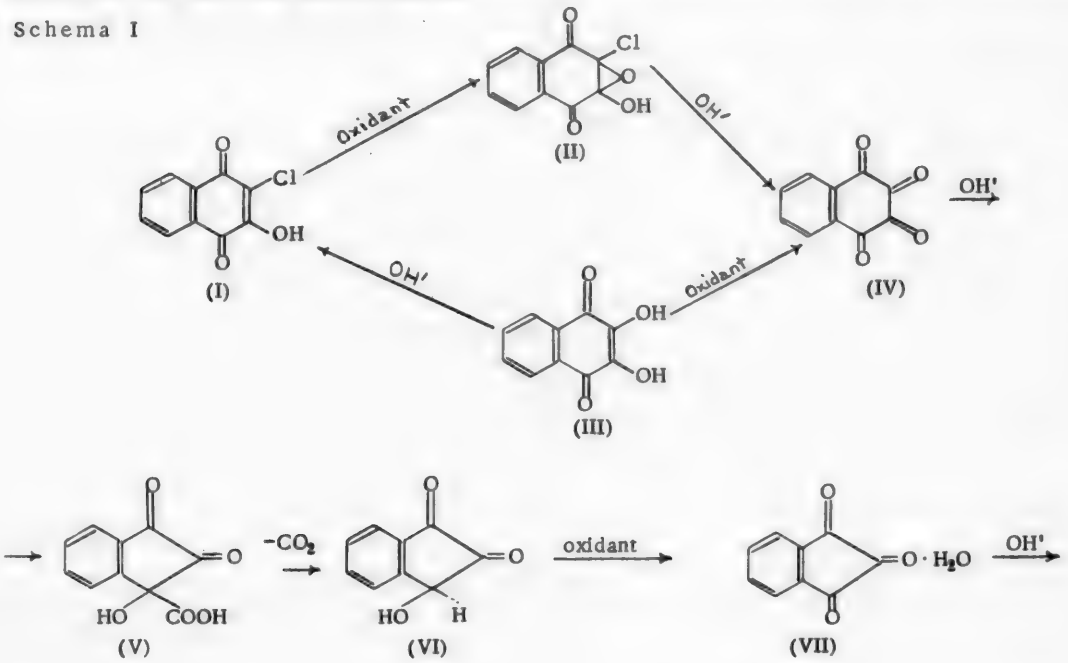
XXIII. The Mechanism Involved in Oxidation-Reduction and Hydrolytic Transformations of 2-Chlorohydroxy-1,4-Naphthoquinone

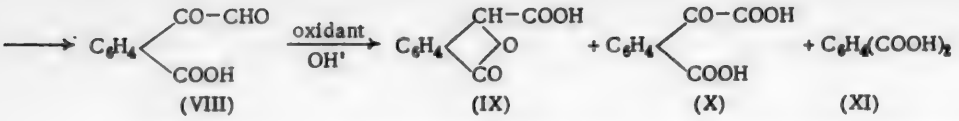
D.P.Vitkovsky and M.M.Shemyakin

We recently showed [1] that when an aqueous alkaline solution of 2-chloro-3-hydroxy-1,4-naphthoquinone (I) is boiled in the absence of atmospheric oxygen, it gradually undergoes profound changes, finally yielding the following compounds: phthalidecarboxylic acid (14%), phthalonic acid (2%), phthalic acid (1%), indanone-1-carboxylic acid-(3) (18%), and 2,3-dihydroxy-1,4-naphthoquinone (56%). We have now discovered another product of the conversion of 2-chloro-3-hydroxy-1,4-naphthoquinone: a red crystalline substance with a m.p. of 315°, the elementary composition of which is given by the empirical formula $C_{27}H_{12}O_3$. When this reaction is carried out with atmospheric oxygen present, the end products comprise only the following of the compounds enumerated above [1]: phthalidecarboxylic acid (52%), phthalonic acid (11%), and phthalic acid (13%).

As for the way in which 2-chloro-3-hydroxy-1,4-naphthoquinone is converted into these three acids, we have already dealt with this problem in one of our preceding reports [1]; it was found that the mechanism involved in the production of these acids is the same whether atmospheric oxygen is present or not. Their formation stems from the fact that 2-chloro-3-hydroxy-1,4-naphthoquinone (I) can be oxidized to 1,2,3,4-tetraoxotetralin (IV) (more precisely, its hydrate) either via the corresponding oxide (II) or via 2,3-dihydroxy-1,4-naphthoquinone (isonaphthazarine) (III), the compound (IV) being converted by the alternating action of oxidizing and hydrolyzing agents, via a series of intermediate steps, into phthalidecarboxylic, phthalonic, and phthalic acids, in accordance with the schema set forth below (see [1,2] for details).

Schema I





(VIII) (IX) (X) (XI)

As we see in Schema I, the formation of the end-product acids from 2-chloro-3-hydroxy-1,4-naphthoquinone entails the necessary participation of an oxidizing agent in three of the intermediate stages of the transformations in question. Whenever the reaction is carried out in the presence of atmospheric oxygen, the latter assumes the role of the oxidant. But the problem of which compound or compounds act as oxidants when the reaction is carried out with atmospheric oxygen excluded (in an atmosphere of nitrogen) has remained moot up to the present time, making it impossible to render a final judgment concerning the nature of the complicated chain of reactions that results in the formation of the substances enumerated above. Inasmuch as a solution of this problem was of interest in comprehending the nature of the oxidative-hydrolytic transformations of carbocyclic compounds, we have devoted the present paper to its elucidation.

We must begin by emphasizing that though nothing but phthalidecarboxylic, phthalonic, and phthalic acids are produced when the process is carried out with atmospheric oxygen present, isonaphthazarine (III), indanone-1-carboxylic acid-(3) (XVII) and a substance with the empirical formula of $C_{27}H_{12}O_3$ (XVIII) are also produced when atmospheric oxygen is excluded. It is sufficiently obvious that the isonaphthazarine arises as the result of the direct substitution of a hydroxyl group for the chlorine atom in the 2-chloro-3-hydroxy-1,4-naphthoquinone molecule under the action of the aqueous alkali solution. Inasmuch as isonaphthazarine is highly stable when no atmospheric oxygen is present [2], it is evident that it is accumulated in very large quantities under these circumstances. Isonaphthazarine can also be produced as an intermediate compound when the reaction is carried out with atmospheric oxygen present, but under these conditions it is converted at a high rate into phthalidecarboxylic, phthalonic, and phthalic acid [2], which explains why it cannot be found among the reaction products in this case as a rule.

We have now established that the following compounds: the initial 2-chloro-3-hydroxy-1,4-naphthoquinone [or more correctly, its tautomeric form (IB)] and the intermediate indenone-1-carboxylic acid (XVI), whose reduction product is the indanone-1-carboxylic acid (XVII) large quantities of which are usually secured, act as oxidants in the oxidative-hydrolytic transformations represented in Schema I when no atmospheric oxygen is present.*

The 2-chloro-3-hydroxy-1,4-naphthoquinone (I) is converted into the terminal acid (XVII) as the result of a ser-series of reducing-hydrolytic and other reactions, represented in Schema II, the experimental basis for which is set forth below. These reducing–hydrolytic reactions parallel the oxidative–hydrolytic transformations shown in Schema I, but are not independent of the latter, which explains the origin of all the substances that can be isolated from the reaction mass after the process is concluded.

The results of our researches have established, therefore, that when an aqueous alkaline solution of 2-chloro-3-hydroxy-1,4-naphthoquinone is boiled with no atmospheric oxygen present, the latter is changed simultaneously in two ways. The first one (Schema I), which is basically oxidative–hydrolytic, results in the formation of phthalidecarboxylic, phthalonic, and phthalic acids, while the second, which is principally reducing–hydrolytic (Schema II) results finally in indanone-1-carboxylic acid-(3) (XVII).** The parallel course of these two processes is due principally to the fact that the initial 2-chloro-3-hydroxy-1,4-naphthoquinone can exhibit the properties of an oxidant as well as a reducer (cf. Schemas I and II). The process later follows two courses for another reason, namely, that the first course of the reaction (Schema I) yields several new reducing agents as intermediate products [isonaphthazarine (III), indanol-3-dione-1,2 (VI), and o-carboxyphenylglyoxal (VIII)], whereas the second course of the process (Schema II) involves the formation of indenone-1-carboxylic acid-(3) (XVI), which can display oxidizing action alongside the chlorotriketone (IB). That is why 2-chloro-3-hydroxy-1,4-naphthoquinone (I) can undergo such far-reaching oxidation–reduction and hydrolytic transformations, the mechanism of which is not yet clear.

Now let us turn to the factual data that justify us in saying that the Schema II set forth below rests on an experimental basis.

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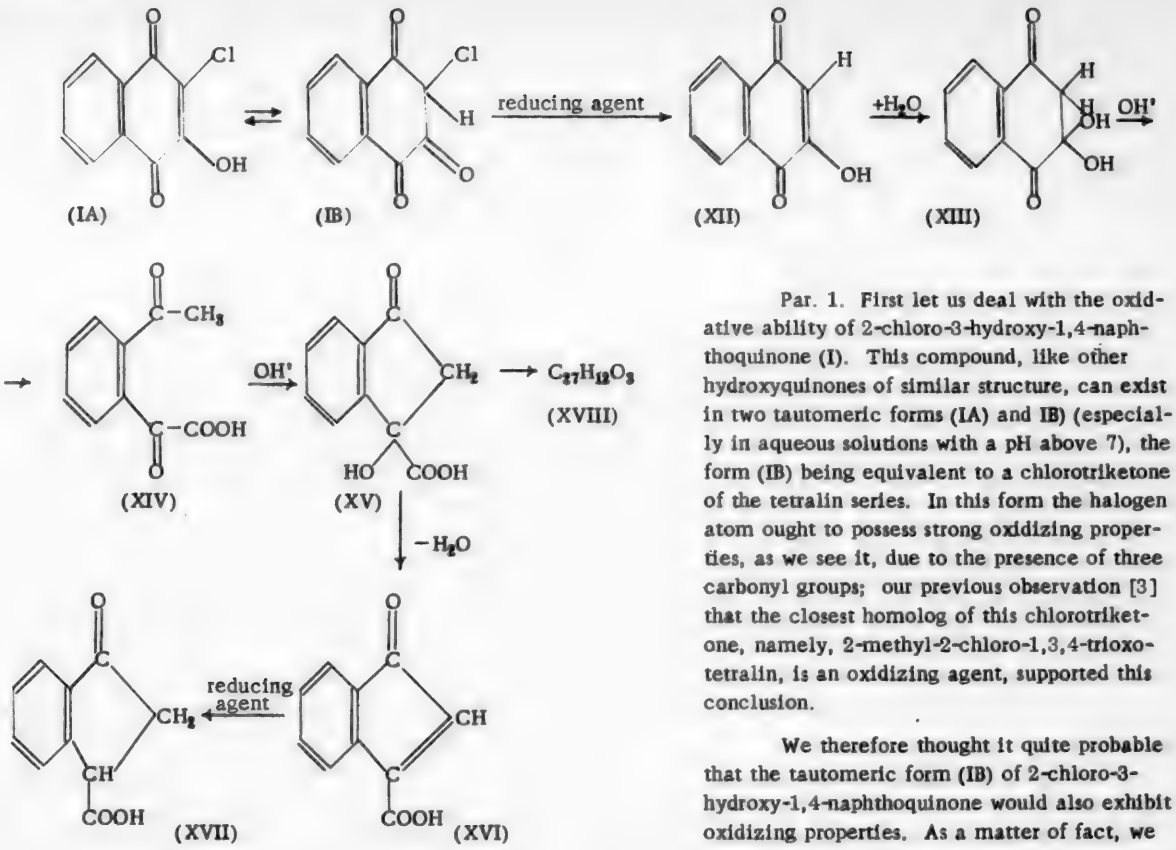
* See [1] for the participation of isonaphthazarine in this process as an oxidant.

** Together with this acid, though apparently due to the action of the oxidant, we get a compound with the empirical formula of $C_{27}H_{12}O_3$ (XVIII).

Schema II



Par. 1. First let us deal with the oxidative ability of 2-chloro-3-hydroxy-1,4-naphthoquinone (I). This compound, like other hydroxyquinones of similar structure, can exist in two tautomeric forms (IA) and IB) (especially in aqueous solutions with a pH above 7), the form (IB) being equivalent to a chlorotriketone of the tetralin series. In this form the halogen atom ought to possess strong oxidizing properties, as we see it, due to the presence of three carbonyl groups; our previous observation [3] that the closest homolog of this chlorotriketone, namely, 2-methyl-2-chloro-1,3,4-trioxotetralin, is an oxidizing agent, supported this conclusion.

We therefore thought it quite probable that the tautomeric form (IB) of 2-chloro-3-hydroxy-1,4-naphthoquinone would also exhibit oxidizing properties. As a matter of fact, we discovered that this quinone can oxidize monovalent negative iodine to free iodine, for example, being itself reduced to 3-hydroxy-1,4-naphthoquinone (XII). On the other hand, we have found that 3-hydroxy-1,4-naphthoquinone (XII) can be converted into indanone-1-carboxylic acid-(3) (XVII) and the compound $C_{27}H_{12}O_3$ (XVIII) under the conditions in which these substances are formed from 2-chloro-3-hydroxy-1,4-naphthoquinone (I).

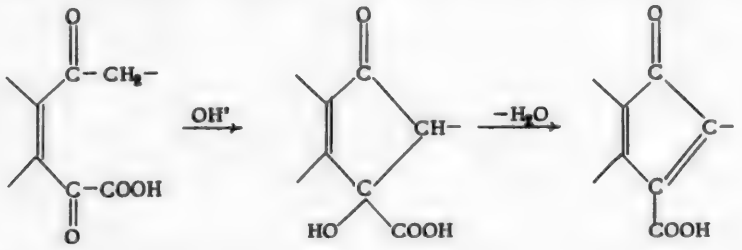
This also proved experimentally that 2-chloro-3-hydroxy-1,4-naphthoquinone (I) possesses oxidizing properties and that 3-hydroxy-1,4-naphthoquinone (XII), the product of its reduction, is the first intermediate substance formed during the conversion of the initial quinone into the final compounds.

Par. 2. As for the second part of the Schema in question (XII) → (XIII) → (XIV), the feasibility and the mechanism of the hydrolytic cleavage of 3-hydroxy-1,4-naphthoquinone (XII) to o-acetylphenylglyoxylic acid (XIV) have been explored previously [4,5], it having been found that this reaction can be carried out with ease in a boiling aqueous solution whose pH is in excess of 7, i.e., under the conditions prevailing during the cleavage of 2-chloro-3-hydroxy-1,4-naphthoquinone (I). It was therefore fairly obvious that o-acetylphenylglyoxylic acid (XIV), like 3-hydroxy-1,4-naphthoquinone (XII), must also be an intermediate product in the transformation of 2-chloro-3-hydroxy-1,4-naphthoquinone (I) into indanone-1-carboxylic acid-(3) (XVII) and the compound $C_{27}H_{12}O_3$ (XVIII). As we have demonstrated experimentally, these two substances are actually produced from o-acetylphenylglyoxylic acid (XIV) under the conditions prevailing when they are secured from 2-chloro-3-hydroxy-1,4-naphthoquinone (I) and 3-hydroxy-1,4-naphthoquinone (XII).

It follows that these transformations are doubtless related to the formation of acetylphenylglyoxylic acid (XIV) as an intermediate product. Hence, both the first and the second parts of Schema II may be regarded as experimentally established.

Par. 3. Now let us turn to consideration of the third part of this schema (XIV) → (XV) → (XVI), dealing with the further changes in o-acetylphenylglyoxylic acid (XIV). As has been noted more than once in our previous

reports [2,4,6-9], diketo acids of this type exhibit a great tendency (particularly when their aqueous– alkaline solutions are heated) to turn into the isomeric cyclic α-hydroxy acids, which in turn can be readily dehydrated, yielding the respective unsaturated acids:



Thus, it has been recently established [7] that the closest homolog of o-acetylphenylglyoxylic acid (XIV), namely, o-propionylphenylglyoxylic acid, is rapidly transformed into 2-methylindenone-1-carboxylic acid-(3) when it is boiled in an aqueous solution whose pH is in excess of 7. There is, therefore, every reason to believe that o-acetylphenylglyoxylic acid (XIV), formed as an intermediate product when 2-chloro-3-hydroxy-1,4-naphthoquinone (I) is boiled in an aqueous solution of an alkali, is likewise converted by the solution, first into the bicyclic α-hydroxy acid (XV) and then into indenone-1-carboxylic acid-(3) (XVI).*

To prove that this part of the schema was correct, we had to show that indenone-1-carboxylic acid-(3) (XVI) can actually be reduced to the final indanone-1-carboxylic acid-(3) (XVII). We carried out the last process, discussed in the following paragraph, under conditions that resembled those used in cleaving the initial 2-chloro-3-hydroxy-1,4-naphthoquinone (I), which was experimental evidence of the correctness of the third part of Schema II.

Par. 4. We used a halogen derivative of indenone-1-carboxylic acid-(3) (XVI) that we had available, namely, 2-chloroindenone-1-carboxylic acid-(3), in our investigation of the reaction of the acid (XVI) (the last part of Schema II).

Isonaphthazarine (III) was selected as the reducing agent, since it is one of the principal intermediate products formed in the course of the transformation of the initial 2-chloro-3-hydroxy-1,4-naphthoquinone (I) into the final phthalidecarboxylic, phthalonic, and phthalic acids (Schema I). The reaction was carried out in an aqueous alkaline solution in an atmosphere of nitrogen, complying with all the conditions required for the formation of these three acids and indanone-1-carboxylic acid-(3) (XVII) from the 2-chloro-3-hydroxy-1,4-naphthoquinone (I). As we expected, we found all the four acids specified above in the reaction solution after the process was complete, whereas the 2-chloroindenone-1-carboxylic acid-(3) yielded no indanone-1-carboxylic acid-(3) (XVII) in a blank test, run without any isonaphthazarine.

Hence, indenone-1-carboxylic acid-(3) (XVI) is actually a predecessor of the final indanone-1-carboxylic acid-(3) (XVII). The latter is produced by the hydrogenation of the indenone-1-carboxylic acid-(3) (XVI) by isonaphthazarine (III) and, evidently, by the other reducing agents [Compounds (VI) and (VIII)] formed during the oxidative–hydrolytic transformation of the initial 2-chloro-3-hydroxy-1,4-naphthoquinone (I) into phthalidecarboxylic, phthalonic, and phthalic acids (see Schemas I and II).

We may thus consider that all the stages of the mechanism we have advanced for the oxidation–reduction and hydrolytic transformations of 2-chloro-3-hydroxy-1,4-naphthoquinone, illustrated in Schemas I and II, have been proved.

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* Apparently the bicyclic α-hydroxy acid (XV) is the ancestor of the substance with the empirical formula of $C_{27}H_{12}O_3$, as well as of the unsaturated acid (XVI). This compound (XVIII) is probably formed by the condensation of three molecules of the α-hydroxy acid (XV), while it is oxidatively decarboxylated at the same time, as is often the case, we know, in cyclic α-hydroxy acids of this sort (cf. [4]):

$$3C_{10}H_8O_4 = C_{27}H_{12}O_3 + 3CO_2 + 3H_2O + 6H\cdot$$
(XV) (XVIII)

In this process the dehydrogenating action is evidently due to the tautomeric form of the initial quinone (IB) and the unsaturated acid (XVI), which is reduced to indanone-1-carboxylic acid-(3) (XVII). The question of the structure of the substance (XVIII) is still unsolved.

EXPERIMENTAL*

1. Transformations of 2-chloro-3-hydroxy-1,4-naphthoquinone in an aqueous solution of an alkali. The reaction was carried out in an atmosphere of nitrogen under the conditions stipulated in Report XXII [10] (experiment 1), 10.4 g (0.05 mole) of the 2-chloro-3-hydroxy-1,4-naphthoquinone being boiled with 5 liters of a 1% aqueous solution of sodium hydroxide for 24 hours. After this heating the reaction mass was cooled in a current of nitrogen, and the precipitate filtered out and washed a few times with hot water. The dried and thoroughly pulverized precipitate was then boiled with 50 ml of chloroform for 30 minutes, the insoluble portion being filtered out, and the filtrate evaporated to a total volume of 2-3 ml. As it cooled, a red crystalline substance (needles) with a m.p. of 309-310° settled out. It weighed 0.06 g (0.9% yield). The m.p. was 315° after recrystallization from alcohol.**

The substance produced was insoluble in alkalis or in dilute acids; it dissolved with some difficulty when heated in chloroform, ether, benzene, xylene, and tetralin.

Found %: C 84.49; H 3.49; M 373 (in phenol). $C_{27}H_{12}O_3$. Calculated %: C 84.37; H 3.13; M 384.

2. The oxidizing ability of 2-chloro-3-hydroxy-1,4-naphthoquinone. a) 0.1417 g of 2-chloro-3-hydroxy-1,4-naphthoquinone was heated in 30 ml of alcohol until it dissolved, after which 30 ml of concentrated hydrochloric acid and 2.0 g of potassium iodide were added to the solution. The mixture was boiled for 45 min, after which it was cooled and 250 ml of water was added. The iodine liberated was titrated back with 0.1 N hyposulfite solution. The iodine totaled 0.1588 g (92%, based on the initial quinone). A similar reaction can be carried out in acetic acid; it is rather slow at room temperature and much faster when heat is applied.

b) 0.50 g of 2-chloro-3-hydroxy-1,4-naphthoquinone was heated in 40 ml of alcohol until it dissolved, and 50 ml of concentrated hydrochloric acid and 3 g of potassium iodide were added to the solution. The mixture was boiled for 45 minutes; when it cooled 200 ml of water was added to it, and then a 5% aqueous solution of sodium bisulfite was added until the iodine color had vanished. The resultant solution was extracted repeatedly with ether, and the ether extract was washed with a concentrated solution of potassium chloride and then with water and dried with calcium chloride. Driving off the ether left behind 0.40 g of a crystalline substance, which was recrystallized twice from a small quantity of alcohol containing activated charcoal. The resultant compound had a m.p. of 190-191° and exhibited no depression of the melting point when mixed with 3-hydroxy-1,4-naphthoquinone. 97% yield.

3. Transformations of 3-hydroxy-1,4-naphthoquinone in an aqueous solution of an alkali. The reaction was carried out in an atmosphere of nitrogen, under the conditions set forth in Report XXII [10] (Experiment 1), 10.44 g (0.06 mole) of 3-hydroxy-1,4-naphthoquinone being boiled for 24 hours with 6 liters of a 1% aqueous solution of sodium hydroxide. Soon after boiling began, a precipitate began to settle out of the reaction solution, its quantity gradually increasing. When heating was over, the reaction mixture was cooled in a current of nitrogen, after which the resultant precipitate was filtered out and washed a few times with hot water. It weighed 2.3 g; the m.p. was 345-370° (the analysis of this substance is described below).

The pH of the solution was brought down to 6.5-7.0 by adding sulfuric acid, and then the solution was evaporated in a current of nitrogen until its volume totaled 400-500 ml. The precipitated silicic acid*** was filtered out, boiled with 20 ml of water, and refiltered, this operation being repeated two more times. The wash waters were combined with the bulk of the filtrate, and conc. sulfuric acid was added until it constituted 10% of the solution; during acidulation an emulsion settled out at first, followed by the formation of a highly tarred precipitate, which was filtered out and washed with water. The filtrate was decolorized with activated charcoal and then extracted 5 times with chloroform. The extract was dried with calcium chloride and filtered, after which the solvent was driven off. This yielded 3.2 g of a dark, noncrystallizing oil, which was heated in 100 ml of water until it dissolved and then boiled with activated charcoal for 10 minutes, after which the charcoal was filtered out. As it cooled, a crystalline precipitate settled out, which was filtered out and air-dried the next day.

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* The analytical portion of this research was carried out with the participation of E.A.Ignatyeva, to whom we are deeply grateful.

** The analysis of the reaction solution is described in Report XVII [1].

*** The silicic acid was produced during the reaction by the action of the alkali solution upon the surface of the glass flask.

It weighed 3.0 g; its m.p. was 81-82°. The m.p. of the substance was raised to 83-84° after recrystallization from water; its mixed melting point with the indanone-1-carboxylic acid-(3) described previously [1] exhibited no depression. Evaporating the aqueous mother liquor yielded a little more of this acid. The acid yield was 29%. No phthalidecarboxylic, phthalonic, or phthalic acid was found in the reaction products.

The substance with a m.p. of 345-370° described above, which was recovered at the end of the reaction, was dissolved in 1.5 liters of boiling chloroform. The solution was evaporated to a volume of about 100 ml, and the resulting precipitate was filtered out. This yielded 0.9 g of a substance as elongated yellow filaments with a m.p. of 371° (this substance was not investigated further). The filtrate was concentrated to a volume of some 50 ml; after it had stood for a long time, orange-red crystals began to settle out (they weighed 3.1 g; m.p. 301-310°). These crystals were recrystallized three times from xylene, twice from tetralin, and once from chloroform, after which their melting point was 315°, the mixed melting point with the compound $C_{27}H_{12}O_8$ secured in Experiment 1 exhibiting no depression.

4. Transformations of o-acetylphenylglyoxylic acid in an aqueous solution of an alkali. The reaction was carried out in an atmosphere of nitrogen under the conditions set forth in Report XXII [10] (Experiment 1), 1.9 g (0.01 mole) of o-acetylphenylglyoxylic acid being boiled for 24 hours with 1 liter of a 1% aqueous solution of sodium hydroxide. The solution, which was colorless at first, soon turned yellow, and then a yellow precipitate began to settle out, constantly increasing in size. After three to four hours had elapsed, the solution turned green. After heating was complete, the reaction mixture was cooled in a current of nitrogen, the precipitate being filtered out and washed a few times on the filter with hot water. It weighed 0.44 g; m.p. 345-370°. The precipitate was dissolved in boiling chloroform, and then the procedure described in Experiment 2 was employed to recover 0.2 g of a yellow substance with a m.p. of 371° and 0.24 g of a red substance with a m.p. of 315° from it. The latter substance was identical with the $C_{27}H_{12}O_8$ compound secured in Experiments 1 and 3.

After the precipitate had been filtered out, sulfuric acid was added to the aqueous reaction solution (until the solution pH was 6.5-7.0), and the latter was evaporated to a volume of about 150 ml and cooled, the precipitated silicic acid being filtered out. The precipitate was washed three times on the filter with small portions of hot water. The wash waters were combined with the bulk of the filtrate, and 20 ml of conc. sulfuric acid was added, throwing down a brown, tarry substance, which was filtered out. The transparent, nearly colorless filtrate was extracted with chloroform, the extract being dried with calcium chloride, and the chloroform driven off. This left 0.7 g of a yellowish oil, which was dissolved in hot water; the solution was boiled for a few minutes with activated charcoal, filtered, and cooled. 0.6 gram of indanone-1-carboxylic acid-(3) with a m.p. of 83-84° was recovered, its yield being 34%. No phthalidecarboxylic, phthalonic, or phthalic acid was found in the reaction products.

5. Reaction of 2-chloroindenone-1-carboxylic acid-(3) with isonaphthazarin. The reaction was carried out in an atmosphere of nitrogen under the conditions described in Report XXII [10] (Experiment 1), a mixture of 10.5 g (0.05 mole) of 2-chloroindenone-1-carboxylic acid-(3) and 1.90 g (0.01 mole) of isonaphthazarin being boiled for 24 hours with 0.5 liter of a 2% aqueous solution of sodium hydroxide. The solution, which was blue at first, soon turned brown, and after a few hours had elapsed, a tarry precipitate began to settle out. After heating was over, the reaction mass was cooled in a current of nitrogen and acidulated with sulfuric acid until its reaction was acid with Congo red, a large quantity of heavily tarred substances settling out. These were filtered out, and the filtrate was repeatedly extracted, first with chloroform and then with ether. The chloroform solution was dried with calcium chloride, and then the solvent was driven off until the volume of the residue totaled 2-3 ml. A very small quantity of phthalidecarboxylic acid, m.p. 151-152° (from water), gradually settled out of the solution. The chloroform mother liquor left after this acid had been filtered out was evaporated to dryness. This left a noncrystallizing oil, which was dissolved in 50 ml of hot water and boiled for a few minutes with activated charcoal, after which the charcoal was filtered out. As the solution cooled, 0.4 g of indanone-1-carboxylic acid-(3) settled out; its m.p. was 83-84° after two recrystallizations from water.

The ether solution secured earlier was evaporated, the residual oil being boiled with 20 ml of water containing activated charcoal, after which the aqueous solution was filtered and extracted with ether. Driving off the ether left an oily substance that gradually crystallized. It was recrystallized twice from water containing activated charcoal. The 0.1 g of phthalic acid recovered had a m.p. of 195-200° with decomposition; heating it above the decomposition temperature converted it into phthalic anhydride with a m.p. of

130°. An extremely small quantity of phthalonic acid, as the corresponding quinoxaline derivative with a m.p. of 237-239° (from alcohol), could be recovered by the method described previously [11] from the aqueous mother liquor left after the recrystallization of the phthalic acid.

SUMMARY

The mechanism of the oxidation-reduction and hydrolytic transformations of 2-chloro-3-hydroxy-1,4-naphthoquinone that take place when it is boiled in an aqueous alkali solution with atmospheric oxygen excluded has been investigated and established experimentally.

It has been found that the phthalidecarboxylic acid, phthalonic acid, phthalic acid, indanone-1-carboxylic acid-(3), isonaphthazarine, and the substance with the empirical formula of $C_{27}H_{18}O_3$ produced under these conditions arise as the result of two parallel interrelated processes, one of which is primarily oxidative-hydrolytic, while the other is reducing-hydrolytic. This complicated chain of transformations ends up in the formation of the end products enumerated above, recovered at the end of the process.

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2) " " " " " p. 1113.

3) " " " " " p. 431.

4) " " " " " p. 997.

5) " " " " " p. 733 (this issue).

6) " " " " " p. 457.

7) " " " " " p. 607.

8) " " " " " p. 739 (this issue).

9) " " " " " p. 381.

XXXVII. THE CONVERSION OF TETRAHYDROFURFURYL ALCOHOL AND TETRAHYDROFURFURYLTHIOL INTO Δ^3-DIHYDROTHIOPYRAN

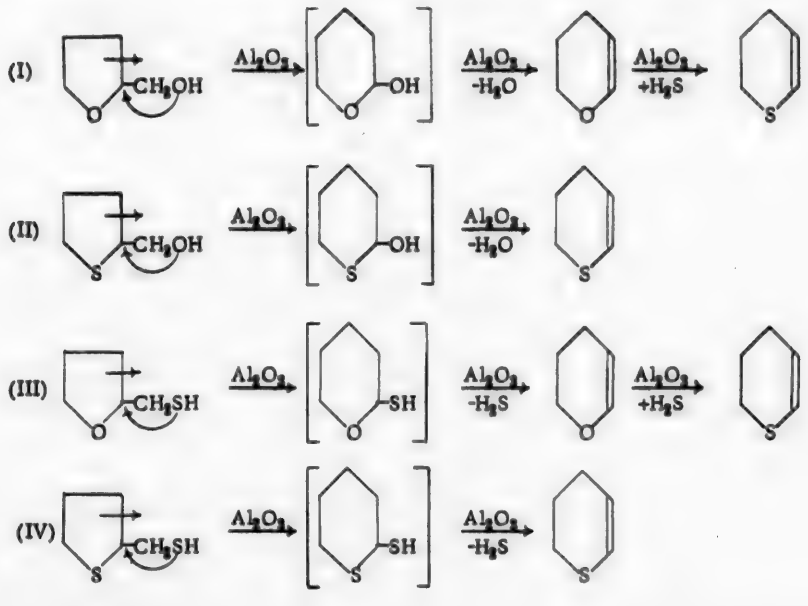
Yu. K. Yuryev and E. G. Vendelshtein

In previous papers one of the present authors has shown that furanidine (tetrahydrofuran) and its homologs are converted into thiophane and the latter's respective homologs [1] by the action of hydrogen sulfide at 250-400° over alumina and that Δ^2-dihydropyran and tetrahydropyran undergo a similar transformation, yielding Δ^3-dihydrothiopyran [2] and tetrahydrothiopyran [3], respectively.

In the present research we have explored the behavior of tetrahydrofurfuryl alcohol in this reaction, and the behavior of tetrahydrofurfurylthiol when in contact with alumina.

Dehydrating tetrahydrofurfuryl alcohol at 300-375° over alumina involves the conversion of the five-membered oxygen-containing ring into a six-membered ring, resulting in the formation of Δ^3-dihydropyran [4]. We therefore expected that reacting tetrahydrofurfuryl alcohol with hydrogen sulfide over alumina would yield Δ^3-dihydrothiopyran, both as the result of the conversion of Δ^2-dihydropyran (Schema I) and, possibly, as the result of dehydration coupled with expansion of the ring of the intermediate α-hydroxymethylthiophane (Schema II). Inasmuch as thiols are produced by the combined catalytic dehydration of alcohols and hydrogen sulfide at 300-380°, it was quite possible that tetrahydrofurfurylthiol and α-mercaptomethylthiophane would be produced as intermediates when tetrahydrofurfuryl alcohol was reacted with hydrogen sulfide.

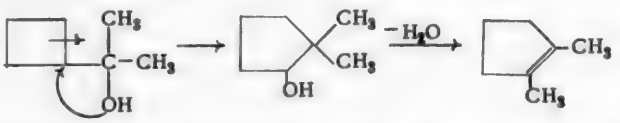
We found earlier that functional derivatives of the furan and furanidine series (alcohols, aldehydes, and ketones [6], and acid esters [7]) are unstable during the catalytic conversion of heterocyclic compounds. We believe that α-hydroxymethylthiophane (Schema II), tetrahydrofurfurylthiol (Schema III), and α-mercaptomethylthiophane (Schema IV) should undergo isomerization, like tetrahydrofurfuryl alcohol (Schema I), when placed in contact with alumina at high temperatures (300-380°), being converted into six-membered heterocyclic compounds with the same hetero atoms and with a hydroxyl or a sulfhydryl group attached to the alpha carbon atom of the ring. Subsequent splitting off of water or hydrogen sulfide from these compounds ought to yield Δ^3-dihydrothiopyran (Schemas II and IV), Δ^3-dihydropyran (Schemas I and III), respectively, the Δ^3-dihydropyran being converted into Δ^3-dihydrothiopyran (Schemas I and III) by its reaction with hydrogen sulfide (either introduced into the reaction or produced therein):



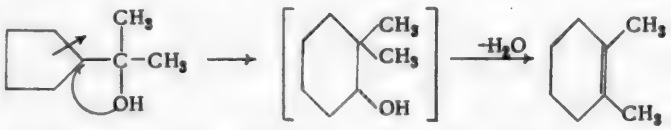
It is highly probable that the reaction can follow the course of Schema III, i.e., with tetrafurfuryl alcohol first giving rise to tetrahydrofurfurylthiol, since we secured Δ^2-dihydrothiopyran by placing tetrahydrofurfurylthiol in contact with alumina at 300° (the reaction was accompanied by the evolution of hydrogen sulfide). Thus, the synthesis of Δ^2-dihydrothiopyran from tetrahydrofurfurylthiol (Schema III)— the conversion of a five-membered oxygen-containing heterocyclic compound into a six-membered sulfur-containing one — seemed to us to be a three-stage process, like the synthesis of Δ^2-dihydropyran from tetrahydrofurfuryl alcohol followed by its conversion into Δ^2-dihydrothiopyran (Schema I).

We believe that the cited schemas of the mechanism involved in the conversion of functional derivatives of saturated five-membered heterocyclic compounds into unsaturated six-membered ones containing the same hetero atoms are more credible and more general than the schema put forward by Paul [5], in which the intermediate stage in the synthesis of Δ^2-dihydropyran from tetrahydrofurfuryl alcohol involves the formation of methylenetetrahydrofuran (by dehydration of the alcohol), which is then isomerized to Δ^2-dihydropyran.

The schema we suggest for the mechanism involved in the expansion of a five-membered oxygen-containing, nitrogen-containing [6], or sulfur-containing heterocyclic compound to a six-membered one is supported and confirmed by one of the papers by N.M.Kizhner, who showed that the action of dehydrating agents upon complex carbinols isomerizes their rings and shifts their radicals. When dimethylcyclobutylcarbinol is reacted with oxalic or dilute sulfuric acid, we get 1,2- rather than 1,1-dimethylcyclopentene-1, the reaction involving the formation of the intermediate 1,1-dimethylcyclopentanol-2 [8]:



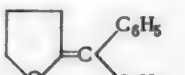
S S. Nametkin has observed a similar phenomenon: when dimethylcyclopentylcarbinol was dehydrated by heating it with oxalic acid (by the N.M.Kizhner method), it yielded 1,2-dimethylcyclohexene-1:



In the instances cited the only possible reason for the shift of the methyl group is a retropinacol conversion of the resulting pinacol cyclic alcohol.

There is, therefore, no doubt that the intermediate substance present during the formation of Δ^2-dihydropyran from tetrahydrofurfuryl alcohol is not methylenetetrahydrofuran (a product of the dehydration of the alcohol), as R. Paul supposes, but α-hydroxytetrahydropyran, a product of the isomerization of the initial alcohol; the latter compound yields Δ^2-dihydropyran upon dehydration (Schema I).

Paul cites [10] the catalytic dehydration of diphenyltetrahydrofurylcarbinol, which does not entail isomerization and stops at the stage in which epoxy-1,4-5,5-diphenylpentene-4 (a compound with a heptacyclic double bond)

 is formed,

as proof of the correctness of the schema given by him for the formation of Δ^2-dihydropyran from tetrahydrofurfuryl alcohol. S.S.Nametkin and M.A.Volodina have shown, however, that diphenylpentylcarbinol is dehydrated to a hydrocarbon containing a heptacyclic double bond, i.e., without any isomerization of the ring, which is in sharp contrast to dimethylcyclopentylcarbinol [11]. We assert that, inasmuch as epoxy-1,4-5,5-diphenylpentene-4, which has a styrene group (as has the dehydration product of diphenylcyclopentylcarbinol), is produced by dehydration of diphenyltetrahydrofurylcarbinol, it is quite obvious that the behavior of diphenyltetrahydrofurylcarbinol cannot be compared with that of tetrahydrofurfuryl alcohol in this reaction.

In the N.M.Kizhner and S.S.Nametkin reactions cited above we have a confirmation of the scheme we propose for the expansion of the ring involved in the splitting out of water from tetrahydrofurfuryl alcohol and α-hydroxymethylthiophane and in the splitting out of hydrogen sulfide from tetrahydrofurfurylthiol and α-mercaptomethylthiophane.

We attribute the absence of this thiol in the product of the reaction of tetrahydrofurfuryl alcohol with hydrogen sulfide to the transformation of the tetrahydrofurfurylthiol into Δ^2-dihydrothiopyran.

The yield of the Δ^2-dihydrothiopyran from the tetrahydrofurfurylthiol drops sharply as the reaction temperature is raised (22% at 300° and 2.3% at 380°); a similar phenomenon takes place when the temperature is raised in the catalytic dehydration of tetrahydrofurfuryl alcohol—in the synthesis of Δ^2-dihydropyran [12]—and in the catalytic synthesis of Δ^2-dihydrothiopyran from tetrahydrofurfuryl alcohol and hydrogen sulfide (27% at 300° and 11% at 350°). In every case decomposition increases sharply as the reaction temperature is raised, the catalyst being covered with a thick layer of carbon-like film.

After the present research had been completed, Naylor [13] published a paper on the use of a similar method in synthesizing Δ^2-dihydrothiopyran from tetrahydrofurfuryl alcohol, which combines in one reaction — as indicated above — the synthesis of Δ^2-dihydropyran [4] and the conversion of the latter into Δ^2-dihydrothiopyran, first described by one of the present authors [2]. The British author did not realize, however, that the transformations of functional derivatives of oxygen-containing heterocyclic compounds into rings containing other hetero atoms take place more easily than the transformations of their parental rings: furan, furanidine, Δ^2-dihydropyran and tetrahydropyran, so that fairly mild temperatures must be employed, avoiding any unnecessary rise in temperature. Naylor secured Δ^2-dihydrothiopyran from Δ^2-dihydropyran as well as from tetrahydrofurfuryl alcohol at excessively high temperatures: 425° and 375°, respectively, and in the presence of activated alumina into the bargain. That is why he secured a low yield of Δ^2-dihydrothiopyran containing tetrahydrothiopyran as an impurity in the first case, while in the second case the yield "was low" and the preparation "was somewhat impure".

Too high temperature and an excessively active catalyst merely promoted decomposition of the substance; the hydrogen evolved during decomposition could be added to the Δ^2-dihydrothiopyran produced by the cited author under such severe conditions, thus giving rise to the small amount of tetrahydrothiopyran found as an impurity in the principal reaction product.

In the present paper, as in the preceding one [2], the Δ^2-dihydrothiopyran was synthesized under much milder conditions. The fractionation data of the reaction products secured by reacting tetrahydrofurfuryl alcohol with hydrogen sulfide in the presence of alumina at 300 and 350° clearly show how this reaction is complicated when the temperature is raised: at 350° first runnings (which may also contain tetrahydrothiopyran) appear, distilling at 139-143.5°, though they are practically absent in the catalyzate secured at 300°.

The transformation of Δ^2-dihydropyran into Δ^2-dihydrothiopyran described earlier was also carried out under milder conditions (375°, unactivated alumina), which made it possible to avoid unnecessary decomposition and to secure Δ^2-dihydrothiopyran [2] containing no tetrahydrothiopyran.

EXPERIMENTAL

Synthesis of tetrahydrofurfurylthiol. The tetrahydrofurfurylthiol was prepared by reacting the sodium salt of tetrahydrofurfurylsulfuric acid with potassium hydrosulfide. 40 g of tetrahydrofurfuryl alcohol was stirred vigorously and chilled while 28 ml of concentrated H_2SO_4 was added. After this chilling of the reaction mass, ice was added to it, and then anhydrous soda (about 40 g) was added portionwise until the reaction was neutral. After the solution of the sodium salt of tetrahydrofurfurylsulfuric acid had stood for 10-15 hours, the crystals of Glauber salt were filtered out, and the filtrate was evaporated until a film appeared and then mixed with a solution of 17 g of potassium hydroxide in 34 ml of water, saturated with hydrogen sulfide. The reaction mixture was refluxed for 6-8 hours on an oil bath, and the reaction products distilled. This yielded a distillate passing over up to 115° and consisting of water and about 10 ml of a heavy colorless oil, which was extracted with ether. The ether extract was re-treated with a potassium hydroxide solution. The alkaline solution of potassium mercaptide was separated, extracted a few times with ether, and acidulated with hydrochloric acid after the ether had been driven off. Distillation of the residue left after the ether solution had been dried with anhydrous Na_2SO_4 and the ether had been driven off yielded 6.0 g of tetrahydrofurfurylthiol, with a b.p. of 167-169° (746 mm).

The residue left in the reaction flask was acidulated with hydrochloric acid. The upper layer was separated and extracted with ether. After the ether had been driven off, the residue was distilled, the distillate collected in the 95-320° range being treated with a solution of potassium hydroxide. The appropriate treatment of an alkaline solution of the potassium mercaptide yielded 1 g of tetrahydrofurfurylthiol, with a b.p. of 167-168° at 744 mm.

After the tetrahydrofurfurylthiol had been redistilled, it had the following constants:

B.p. 170-170.5° at 752 mm; n_D^{20} 1.4875; d_4^{20} 1.0383; MR_D 32.76; calculated 32.42.
Found %: C 50.87, 50.84; H 8.50, 8.49; S 27.05, 27.03. $C_5H_{10}OS$. Calc.%: C 50.82; H 8.52; S 27.12.

The yield was 6.5 g (14% of the theoretical). Tetrahydrofurfurylthiol is not described in the literature.

Synthesis of Δ^2-dihydrothiopyran from tetrahydrofurfuryl alcohol. a) 110 g of tetrahydrofurfuryl alcohol was passed over alumina at 300° in a current of hydrogen sulfide at the rate of 7-8 drops per minute. The resulting catalyzate was saturated with potassium hydroxide. After the alkaline solution had been separated, the catalyzate was again treated with a solution of potassium hydroxide and then extracted with ether. The ether extract of the catalyzate was dried with calcium chloride, the ether driven off, and the residue distilled into a column with an efficiency of 18 theoretical trays, which yielded the following fractions: I) b.p. 90-139°, 4.5 g; II) b.p. 139-143.5°, 0.1 g; III) b.p. 143.5-144° at 742 mm, 29 g; IV) 144-170°, 2 g; and V) b.p. 170-220°, 3.5 g. The residue left in the flask (21 g) consisted of tar.

Fraction III was Δ^2-dihydrothiopyran:

B.p. 143.5-144° at 742 mm; n_D^{20} 1.5318; d_4^{20} 1.0221; MR_D 30.35; calculated 30.59. Melting point of the $HgCl_2$ compound (in alcohol) 109-110°.

Found %: C 59.91; 60.00; H 8.01, 8.03; S 31.95, 31.92. C_5H_8S. Calc.%: C 59.95; H 8.05; S 32.01.

The yield was 29 g (27% of the theoretical).

Figures in the literature for Δ^2-dihydrothiopyran: Yu.K.Yuryev, T.B.Dubrovina, and E.P.Tregubov [2]: b.p. 143.6-144.2 at 743 mm; n_D^{20} 1.5328; d_4^{20} 1.0244.

The alkali solution with which the catalyzate had been treated was acidulated with hydrochloric acid and extracted with ether. The ether extract was dried with anhydrous Na_2SO_4, and the ether was driven off, leaving 0.1 g of a substance that did not exhibit a reaction for the sulfhydryl group. Hence, the catalyzate did not contain a thiol.

b) 200 g of tetrahydrofurfuryl alcohol was passed over alumina at 350° in a current of hydrogen sulfide at 7-8 drops/min. This yielded 138 g of catalyzate, which was processed as described above and then distilled into a column with an efficiency of 18 theoretical trays. Double fractionation yielded the following fractions: I) b.p. 76-110°, 5 g; II) b.p. 110-125°, 3 g; III) 125-139°, 0.6 g; IV) b.p. 139-143.5°, 3.5 g; V) b.p. 143.5-145°, 21 g; VI) b.p. 145-153°, 2 g; VII) b.p. 153-174°, 0.8 g. The residue in the flask, tar, totaled 32 g.

Fraction V was Δ^2-dihydrothiopyran (11% of the theoretical yield), b.p. 143.5-145° (755 mm); n_D^{20} 1.5328; d_4^{20} 1.0212; the $HgCl_2$ compound had a melting point (from alcohol) of 109-110°.

Conversion of tetrahydrofurfurylthiol into Δ^2-dihydrothiopyran. a) 27 g of tetrahydrofurfurylthiol was passed over alumina at 300° in a current of nitrogen at the rate of 7-8 drops/min. The 12.5 g of catalyzate was extracted with ether. After the ether extract had been dried with anhydrous Na_2SO_4 and the ether had been driven off, distillation of the reaction product from a flask fitted with a dephlegmator yielded the following fractions: I) b.p. 115-139°, 6.4 g; II) b.p. 139-148°, 5.4 g; III) b.p. 148-220°, 6.1 g. Redistillation of Fractions I and II into a column with an efficiency of 18 theoretical trays yielded 5.2 g of Δ^2-dihydrothiopyran (22% of the theoretical yield):

B.p. 143-144.5° at 742 mm; n_D^{20} 1.5318; d_4^{20} 1.0232. M.p. of the $HgCl_2$ compound (from alcohol): 109-110°.

Found %: C 59.98, 59.92; H 8.00, 7.97; S 31.89, 31.94. C_5H_8S. Calc.%: C 59.95; H 8.05; S 32.01.

b) 20 g of tetrahydrofurfurylthiol was passed over alumina at 380° in a current of nitrogen (at a rate of 7-8 drops/min.) After the gaseous reaction products had passed through a wash bottle filled with sodium plumbite, they were collected in a gasometer. The abundant black precipitate of lead sulfide indicated that hydrogen sulfide was present in the gases. 2300 ml of gas was collected (after the nitrogen introduced had been deducted). The 7.6 g of catalyzate was treated as in the preceding experiment. Redistillation of the reaction product from a flask fitted with a dephlegmator yielded 0.4 g of Δ^2-dihydrothiopyran (2.3% of the theoretical yield).

B.p. 143-144.5° at 745 mm; n_D^{20} 1.5312; d_4^{20} 1.0216. M.p. of the $HgCl_2$ compound (from alcohol) 109-110°.

Analysis of the gaseous reaction products yielded the following results: 42.4% unsaturated hydrocarbons; 20.2% saturated hydrocarbons; 37.2% carbon monoxide.

SUMMARY

1. When tetrahydrofurfuryl alcohol is reacted with hydrogen sulfide above alumina at 300°, the ring is first expanded, Δ^2-dihydropyran being produced; the action of hydrogen sulfide upon the latter converts it into Δ^2-dihydrothiopyran.

2. When tetrahydrofurfurylthiol is brought into contact with alumina at 300°, its ring is expanded, yielding Δ^2-dihydrothiopyran.

3. The functional derivatives of the furanidine series – tetrahydrofurfuryl alcohol and tetrahydrofurfurylthiol – are transformed at lower temperatures and, hence, more readily than the transformations of furanidine (tetrahydrofuran) and of its homologs.

4. The rings of the five-membered heterocyclic compounds that contain functional groups – tetrahydrofurfuryl alcohol, tetrahydrofurfurylthiol, α-hydroxymethylthiophane, and α-mercaptomethylthiophane – are expanded when they are brought into contact with alumina in accordance with a mechanism that holds good for them all: first, isomerization to a six-membered heterocyclic compound with the same hetero atom and with a hydroxyl or sulfhydryl group attached to the α-carbon atom, followed by splitting out of a molecule of water or hydrogen sulfide, respectively, yielding a six-membered Δ^2-unsaturated heterocyclic compound containing the same hetero atom.

When the hydrogen sulfide is split out from the tetrahydrofurfurylthiol, it reacts at once with the resultant Δ^2-dihydropyran in the presence of Al_2O_3, substituting sulfur for the oxygen. This is how Δ^2-dihydrothiopyran is formed from tetrahydrofurfurylthiol by placing the latter in contact with Al_2O_3.

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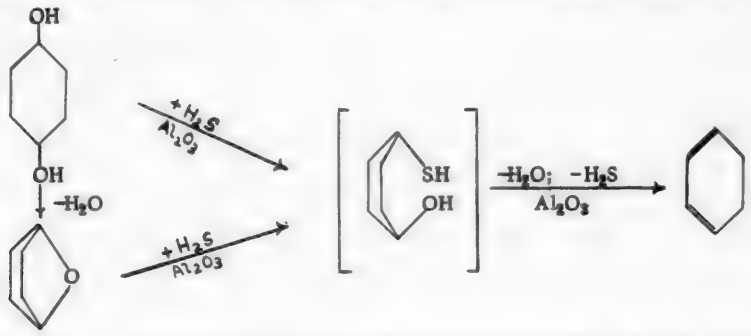
THE CATALYTIC DEHYDRATION OF 1,4-ENDOXOCYCLOHEXANE AND 1,4-DIHYDROXYCYCLOHEXANE IN AN ATMOSPHERE OF HYDROGEN SULFIDE

Yu K Yuryev, G.Ya Kondratyeva, and E.P.Smyslova

In our previous reports we have found that 2,2,5,5-tetramethylfuranidine is converted into 2,5-dimethylhexadiene-2,4 (diisocrotyl), a diene hydrocarbon with conjugated double bonds, instead of 2,2,5,5-tetramethylthiophane, by reacting it with hydrogen sulfide over alumina at 350° [1]. When 2,2,5,5-tetramethylfuranidine was dehydrated catalytically under the same conditions, but with hydrogen sulfide absent, we got a mixture that contained 2,5-dimethylhexadiene-1,5 (diisobutenyl), 2,5-dimethylhexene-2 (the cis and trans isomers), and possibly 2,5-dimethylhexane, in addition to 2,5-dimethylhexadiene-2,4 [2]. We were unable to separate the hydrocarbon mixture into its components, even by distilling the reaction product twice into a column with an efficiency of 25 theoretical trays, and the composition of the mixture was investigated by analyzing the Raman spectra of narrow fractions.

In the present research we made a study of the joint dehydration of 1,4-endoxocyclo- and 1,4-dihydroxycyclohexane with hydrogen sulfide over alumina with the objective of synthesizing 1,4-endothiocyclohexane. Even in this case, however, we secured a diene hydrocarbon, cyclohexadiene-1,3, rather than a sulfur-containing heterocyclic compound. Apparently, as in the case of 2,2,5,5-tetramethylfuranidine, which is formed as an intermediate from 1,4-endoxocyclohexane and 1,4-dihydroxycyclohexane (by the action of hydrogen sulfide), the disecondary mercapto hydroxy compound split out both water and hydrogen sulfide, yielding cyclohexadiene-1,3:



The impossibility of producing 1,4-endothiocyclohexane in the reactions described above is apparently due to the potential arising in a bicyclic molecule when the bridge oxygen is replaced by sulfur, which has a larger atomic radius.

EXPERIMENTAL

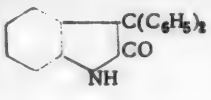
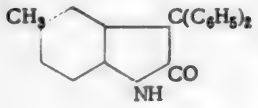
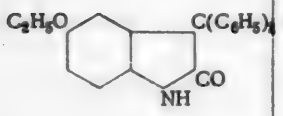
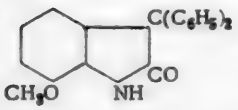
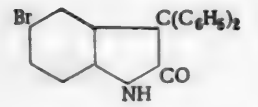
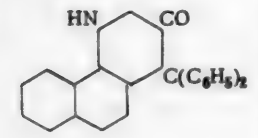
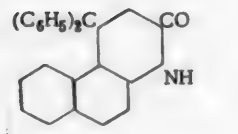
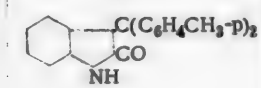
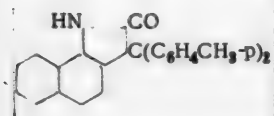
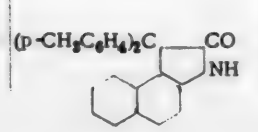
1,4-Endoxocyclohexane was produced by dehydrating 1,4-cyclohexanediol over alumina. 22 g of 1,4-cyclohexanediol and 15 g of Al_2O_3 were heated to 240-250° for 20 hours on an oil bath; the reaction product distilled slowly, drop by drop, into the receiver. The distillate was saturated with potash and extracted with ether. The ether was driven off, the ether extract dried with fused potash, and the residue distilled from a flask with a dephlegmator. 22 g of 1,4-dihydroxycyclohexane yielded 9 g of the crude oxide (48 % of the theoretical yield) with a b.p. of 115-119° at 735 mm. Redistillation of 45 g of the oxide over sodium yielded 42 g of pure 1,4-endoxocyclohexane:

B.p. 118.118.5 at 748 mm; n_D^{20} 1.4490; d_4^{20} 0.9731; MR_D 27.05. $C_6H_{10}O$. Calculated: MR_D 27.15.

Data in the literature for 1,4-endoxocyclohexane: b.p. 120.1°; n_D^{20} 1.4477; d_4^{20} 0.9707 [3].

The same yield of 1,4-endoxocyclohexane was secured when a mixture of 1,4-dihydroxycyclohexane and methanol was passed over alumina [3].

Catalytic dehydration of 1,4-endoxocyclohexane in an atmosphere of hydrogen sulfide. 10 g of 1,4-endoxocyclohexane was passed over alumina at 275° in a current of hydrogen sulfide at a rate of 18 ml per hour. The resultant catalyzate was extracted with ether; the ether extract was washed with a solution of sodium hydroxide and then dried with calcium chloride. After the ether was driven off, the residue was distilled twice from a flask fitted

No.	Formula	M.p.	M.p. of the product obtained in H_2SO_4
1		225°	225-226°
2		198	197.5-198.5
3		250	250
4		270	270
5		284	284
6		253	254
7		266	266
8		200	200-201
9		220	220
10		246.5	246.5

intensity gradually increased. The reaction mass was heated for 10-15 min on a water bath until the crimson coloration disappeared completely. After the mixture had cooled the precipitate was filtered out and recrystallized from acetic acid. Colorless little stars with a m.p. of 270° [1]. Their mixed melting point with a known sample exhibited no depression. The yield was 0.5 g, or 59% of the theoretical.

Anilide of diphenylchloroacetic acid (Experiment 3). 4 ml of phosphorus oxychloride was poured over 4 g of benzilanilide, and the mixture was carefully heated on a water bath until dissolution was complete. When the reaction mass had cooled, it was poured into 100 ml of cold water, the resulting oil crystallizing when the mixture was stirred. This yielded 3 g or 70% of the theoretical. Crystallization from benzene yielded colorless needles with a m.p. of 88°. Klinger gives 88° [2]. The anilide dissolves in concentrated sulfuric acid, giving off hydrogen chloride and turning red, the color disappearing upon standing.

Found %. N 4.3; Cl 11.12. $C_{20}H_{16}ONCl$.

Calculated %: N 4.35; Cl 11.04.

The β-naphthalide of diphenylchloroacetic acid (Experiment 4). 2.5 g of the β-naphthalide of benzilic acid and 2.5 ml of phosphorus oxychloride were used for this reaction. The naphthalide dissolves with difficulty in cold gasoline, but readily in hot; it is soluble in benzene and carbon tetrachloride. It colors concentrated sulfuric acid a transient red-brown. Decolorization is accompanied by the evolution of hydrogen chloride. Triple crystallization from gasoline yielded colorless needles with a m.p. of 109°. The yield was 0.7 g, or 26.9% of the theoretical. The initial β-naphthalide of benzilic acid is produced when an aqueous suspension of the substance is allowed to stand at room temperature, this reaction being accelerated by heat.

0.2650 g substance: 13.8 ml 0.05 N H_2SO_4. 0.0643 g substance: 17.5 ml 0.01 N $AgNO_3$. Found %: N 3.64; Cl 9.66. $C_{24}H_{18}ONCl$. Calculated %: N 3.77; Cl 9.55.

SUMMARY

1. $AlCl_3$, $ZnCl_2$, HSO_3Cl, $POCl_3$, $(CH_3CO)_2O$ and CH_3COCl have been tested as condensing agents for converting the aryl amides of α-hydroxy carboxylic acids into heterocyclic compounds. It was found that anhydrous zinc chloride could be employed for this purpose. In contrast to sulfuric acid, however, the reaction with this chloride requires a higher temperature, while the product's purity and yield are lower. The aryl amides that form halochromic salts with hydrochloric or phosphoric acids are condensed by phosphorus chloride.

2. The reaction of phosphorus oxychloride with the anilide and β-naphthalide of benzilic acid indicates that the aryl amides of diphenylchloroacetic acid can be produced.

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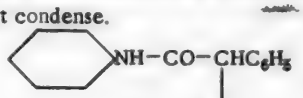
THE N-ARYL AMIDES OF HYDROXY CARBOXYLIC ACIDS AND THEIR CONVERSION INTO HETEROCYCLIC COMPOUNDS

XIV. THE BOUNDARIES OF THE INTRAMOLECULAR CONDENSATION OF ARYL AMIDES OF HYDROXY CARBOXYLIC ACIDS

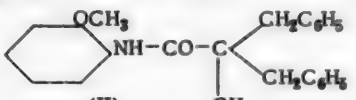
P. A. Petyunin

Aryl amides of rigidly specified structure enter into intramolecular condensations. The ability of aryl amides to enter into condensations is chiefly governed by the nature of the radicals attached to the carbinol carbon atom. The aryl amides of aliphatic α-hydroxy carboxylic acids do not condense, for example. Experiments were made with the anilides of glycolic and diisoamylglycolic acids. Concentrated sulfuric acid was added to an acetic acid solution of diisoamylglycolanilide, and the reaction mass was either allowed to stand for 12 hours at room temperature or heated for 1 hour on a water bath. In the first case the original aryl amide was recovered, while in the second hydrolysis occurred, yielding diisoamylglycolic acid and aniline. Experiments with glycolanilide yielded similar results. Moreover, fusing the latter with anhydrous zinc chloride likewise failed to yield satisfactory results.

The aryl amides of hydroxy carboxylic acids in which one aromatic radical is attached to the carbonyl carbon atom (I) or in which there is no direct bond between the carbinol carbon atom and the benzene rings of the radicals (II), do not condense.



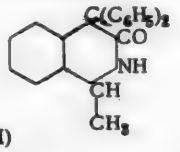
(I)



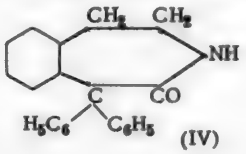
(II)

These aryl amides do not color concentrated sulfuric acid.

Numerous experiments have shown that the aryl amides that form halochromic salts with concentrated sulfuric acid do enter into condensation reactions. Hence, the ability of aryl amides to enter into intramolecular condensations may be governed by the presence of coloration with concentrated sulfuric acid. The α- and β-phenylethylamides of benzilic acid we have synthesized, for instance, produce ephemeral brown and dark-red colorations with concentrated sulfuric acid. When these experiments were carried out preparatively, we secured 1-methyl-4,4-diphenyl-3-oxo-1,2,3,4-tetrahydroisoquinoline (I) and 1,1-diphenyl-2-oxohomotetrahydroisoquinoline (IV):



(III)



(IV)

Of the aryl amides of various hydroxy carboxylic acids we have tested, the compounds of the (VIII), (IX), and (X) types enter into intramoledular condensation. [See next page for (V) to (X)].

EXPERIMENTAL

Ethyl ester of α-phenylethyloxamic acid. When 16 g of α-phenylethylamine, prepared from acetophenone and ammonium formate [1], was mixed together with 24 g of ethyl oxalate, heat was evolved and a small crystalline precipitate was thrown down. Finally, the reaction mass was heated until its reaction was neutral. The contents of the flask were then poured into 50 ml of alcohol, and the precipitated di-(α-phenylethyl)-amide of oxalic acid was processed in the usual manner, yielding 2 g of the substance. The latter is insoluble in water, slightly soluble

in alcohol and carbon tetrachloride, and freely soluble in acetic acid and toluene. It crystallizes from toluene as colorless needles with a m.p. of 195°. The literature gives the m.p. of the di-(α-phenylethyl)-amide of oxalic acid as 180-185° [2]. Driving off the alcohol left behind an oily liquid, which was distilled in vacuo at 213-215° (21 mm). It crystallized when allowed to stand overnight. Colorless needles (from benzene) with a m.p. of 51.5°. The yield was 10.5 g, of 38.2% of the theoretical. The ester is insoluble in water, though soluble in the usual organic solvents. The ethyl ester of α-phenylethyloxamic acid is not described in the literature.

0.2200 g substance: 20.4 ml 0.05 N H_2SO_4. Found%: N 6.48. $C_{12}H_{15}O_3N$. Calculated%: N 6.33.

Ethyl ester of β-phenylethyloxamic acid. 12 g of ethyl oxalate was added to a solution of 8 g of β-phenylethylamine in 20 ml of alcohol. The reaction was completed by heating the flask's contents on a water bath until they no longer manifested an alkaline reaction with litmus paper. This yielded 0.4 g of di-(β-phenylethyl)-amide of oxalic acid. Colorless needles (from alcohol) with a m.p. of 186°. The literature gives the m.p. as 186° [3].

Found%: N 9.29. $C_{18}H_{20}O_2N_2$. Calculated %: N 9.46.

The ethyl ester of β-phenylethyloxamic acid is insoluble in water, slightly soluble in gasoline, and readily soluble in other organic solvents. Colorless needles (from benzene) with a m.p. of 68°. The yield totalled 9 g, or 54.8% of the theoretical.

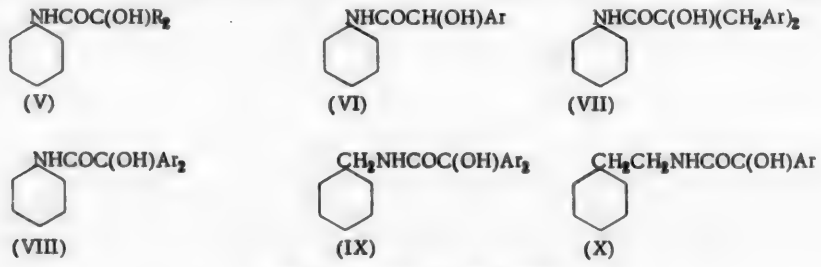
0.1302 g substance: 11.5 ml 0.05 N H_2SO_4. Found%: N 6.11. $C_{12}H_{15}O_3N$. Calculated%: N 6.33.

The o-aniside of dibenzylglycolic acid. We used 4.5 g of the ethyl ester of o-methoxyoxanilic acid, 10.1 g of benzyl chloride, and 1.9 g of magnesium for this reaction. The aniside is insoluble in water and freely soluble in ordinary organic solvents. It does not color concentrated sulfuric acid. Crystallization from alcohol yielded a finely crystalline powder with a m.p. of 150-151°. The yield totaled 4.1 g, or 55% of the theoretical.

0.1916 g substance: 5.28 ml 0.1 N H_2SO_4. 0.2371 g substance: 6.8 ml 0.1 N H_2SO_4. Found%: N 3.86, 4.01. $C_{23}H_{23}O_3N$. Calculated%: N 3.88.

α-Phenylethylamide of benzilic acid. 4 g of the ethyl ester of β-phenylethyloxamic acid dissolved in 30 ml of absolute ether was reacted with phenylmagnesium bromide, prepared from 17 g of bromobenzene and 2.58 g of magnesium in 40 ml of ether. The yield of the recrystallized product totaled 3.7 g, or 58.3% of the theoretical. The substance is insoluble in water or gasoline, though freely soluble in alcohol, ether, and benzene. It colors concentrated sulfuric acid an ephemeral brown. It crystallizes from alcohol as colorless needles with a m.p. of 149.5-150.5°.

0.1448 g substance: 0.4217 g CO_2; 0.0832 g H_2O. 0.1035 g substance: 0.3012 g CO_2; 0.0601 g H_2O. 0.3956 g substance: 24.96 ml 0.05 N H_2SO_4. 0.1803 g substance: 10.9 ml 0.05 N H_2SO_4. Found %: C 79.47, 79.42; H 6.43, 6.5; N 4.39, 4.24. $C_{22}H_{21}O_2N$. Calculated %: C 79.72; H 6.39; N 4.23.



(R = H, alkyl; Ar = aryl).

β-Phenylethylamide of benzilic acid. Initial substances: 6 g of the ethyl ester of β-phenylethyloxamic acid, 33 g of iodobenzene, and 4 g of magnesium. The anilide is insoluble in water, slightly soluble in gasoline, and freely soluble in other organic solvents. It colors concentrated sulfuric acid dark red, the color changing to pale green. It crystallizes from alcohol as colorless lamellae with a m.p. of 139°. The yield totaled 5.3 g, or 65.7% of the theoretical.

0.1531 g substance: 0.4470 g CO_2; 0.0874 g H_2O. 0.1371 g substance: 0.4000 g CO_2; 0.0780 g H_2O. 0.1733 g substance: 10.4 ml 0.05 N H_2SO_4. 0.1926 g substance: 12.3 ml 0.05 N H_2SO_4. Found %: C 79.68, 79.62; H 6.39, 6.37; N 4.32, 4.47. $C_{22}H_{21}O_2N$. Calculated %: C 79.72; H 6.39; N 4.23.

1-Methyl-4,4-diphenyl-3-oxo-1,2,3,4-tetrahydroisoquinoline. 3 g of the α-phenylethylamide of benzilic acid was dissolved in 30 ml of glacial acetic acid, and 15 ml of concentrated sulfuric acid was added to the solution. After the red-brown coloration had disappeared, the reaction product was isolated in the usual manner. The substance is insoluble in water, slightly soluble in benzene, toluene, and gasoline, and readily soluble in alcohol and acetic acid. It crystallizes from dilute acetic acid as colorless rods with a m.p. of 272°.

0.1635 g substance: 0.5047 g CO_2; 0.0869 g H_2O. 0.1802 g substance: 0.5551 g CO_2; 0.0967 g H_2O. 0.1628 g substance: 10.12 ml 0.05 N H_2SO_4. 0.1876 g substance: 12 ml 0.05 N H_2SO_4. 0.0094 g substance: 0.1490 g camphor: Δt 8°. 0.0091 g substance; 0.1100 g camphor: Δt 10.8°. Found %: C 84.29, 84.06; H 5.95, 6; N 4.35, 4.48; M 315.5, 306.4. $C_{22}H_{19}ON$. Calculated %: C 84.4; H 6.12; N 4.47; M 313.

Lactam of o-(β-aminoethyl)-triphenylacetic acid (1,1-diphenyl-2-oxohomotetrahydroisoquinoline-symmetrical). Initial substances: a solution of 3.5 g of the β-phenylethylamide of benzilic acid in 20 ml of glacial acetic acid and 30 ml of concentrated sulfuric acid. Condensation was effected at 50-60°. The substance is insoluble in water, though it dissolves in most of the ordinary organic solvents. It crystallizes from alcohol as thin colorless needles with a m.p. of 187-189°. The yield totaled 2.7 g, or 84.6% of the theoretical.

0.1250 g substance: 0.3861 g CO_2; 0.0672 g H_2O. 0.1530 g substance: 0.4740 g CO_2; 0.0832 g H_2O. 0.2359 g substance: 14.5 ml 0.05 N H_2SO_4. 0.1761 g substance: 10.7 ml 0.05 N H_2SO_4. 0.0090 g substance: 0.0986 g camphor; Δt 11.8°. 0.0096 g substance; 0.1011 g camphor: Δt 12.4°. Found %: C 84.29, 84.55; H 5.97, 6.09; N 4.31, 425; M 309.6, 306.2. $C_{22}H_{19}ON$. Calculated %: C 84.4; H 6.12; N 4.47; M 313.

SUMMARY

The proximate boundaries of the intramolecular condensation of the N-aryl amides of hydroxy carboxylic acids have been determined, in so far as the nature of the radicals attached to the carbinol carbon atom are concerned.

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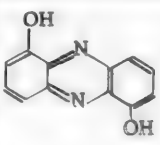
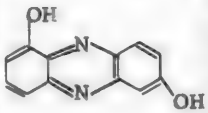
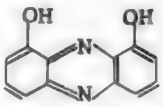
SYNTHESIS OF 1-HYDROXYPHENAZINE DERIVATIVES

III. 1,5-, 1,6-, AND 1,8-DIHYDROXYPHENAZINES

S.E.Serebryany

Not much research has been done on the dihydroxyphenazines. Three of the ten possible isomers have been described in the literature: the 1,2- [1], 2,3- [2], and 1,4-dihydroxyphenazines [3]. It has recently been shown [4,6] that the dihydroxyphenazine produced by hydrogenating iodinin catalytically is 1,5-dihydroxyphenazine [5]. The synthesis of 1,5-, 1,6-, and 1.8-dihydroxyphenazines is described in the present report. We secured these preparations by dealkylating the respective dialkoxyphenazines described by us earlier [6,7]. The properties of the new dihydroxyphenazines are given in the table.

No.	Name	Formula	M.p.	M.p. of the diacetyl derivative
I	1,5-Dihydroxyphenazine		280-281°	240-241°
II	1,6-Dihydroxyphenazine		305-306 (with decomposition)	148-149
III	1,8-Dihydroxyphenazine		296-297 (with decomposition)	257-258

The dihydroxyphenazines listed in the table are well-crystallized substances. They dissolve with very great difficulty in water and fairly difficultly in cold alcohol and benzene. When they are dissolved in dilute alkalies, they produce orange and red phenazinolates. Adding ferric chloride to an alcoholic solution of 1,5-dihydroxyphenazine colors it green. Solutions of the dihydroxyphenazines in dilute mineral acids are orange and red.

The phenazinols readily form well-crystallized diacetyl derivatives.

We are indebted to Prof.A.I. Kiprianov for his valuable counsel.

EXPERIMENTAL*

1,5-Dihydroxyphenazine. 1.8 g of 1,5-diethoxyphenazine, with a m.p. of 184-186° [6] was heated for 5 hours to 130-140° in a sealed tube together with 24 ml of 45% hydrobromic acid. The reaction mixture was treated with an excess of a 10% sodium hydroxide solution, thus producing a cherry-red phenazinolate. The solution was heated to boiling, filtered, and treated with an excess of 30% acetic acid. The dihydroxyphenazine settled out as a yellow-green amorphous precipitate. The precipitate was filtered out and dried. The contaminated product was refined by converting it into a diacetyl derivative. The crude dihydroxyphenazine was boiled with 8 ml of acetic anhydride. Upon cooling the diacetoxyphenazine crystallized as yellow needles with a greenish tinge. The yield was 1.5 g of the substance, with a m.p. of 228-230°. After the acetic anhydride had been driven off, the mother liquor yielded another 0.1 g of the diacetate with a m.p. of 226-230°. The 1,5-diacetoxyphenazine was refined by crystallizing it from alcohol, 1.6 g of the contaminated diacetate yielding 1.4 g of the pure substance with a m.p. of 232-234°. This product was reconverted into 1,5-dihydroxyphenazine by saponifying it with an aqueous solution of an alkali. 1.4 g of the 1,5-diacetoxyphenazine and 15 ml of alcohol were boiled with 75 ml of a 5% sodium hydroxide solution. The precipitate dissolved within 30 minutes, the solution turning cherry-red. The hot solution was filtered and treated with a slight excess of acetic acid. The 1,5-dihydroxyphenazine crystallized as minute yellow needles. They were filtered out, washed with water, and dried. The yield totaled 0.95 g, or 70%, based on the diethoxyphenazine used.

* The melting points of the pure preparations are corrected.

Crystallization from benzene yielded 0.86 g of pure 1,5-dihydroxyphenazine. Golden-yellow needles with a m.p. of 280-281° (in a sealed capillary).

Found %: N 13.24, 13.40. $C_{12}H_8O_2N_2$. Calculated %: N 13.2.

The pure 1,5-dihydroxyphenazine was converted into its diacetyl derivative, 0.18 g of the dihydroxyphenazine yielding 0.23 g of the diacetate with a m.p. of 234-235°. The preparation was recrystallized from alcohol for analysis. Light-yellow needles with a m.p. of 240-241°.

Found %: N 9.55, 9.61. $C_{16}H_{12}O_4N_2$. Calculated %: N 9.46.

1,5-Dihydroxyphenazine can also be produced, with a high yield, by dealkylating a 1,5-dialkoxyphenazine with 65-70% sulfuric acid. 0.9 gram of 1,5-diethoxyphenazine, with a m.p. of 182-184°, was dissolved in 27 ml of 70% sulfuric acid. The solution was refluxed on a paraffin bath at 176-180° for 30 minutes. Upon cooling, the solution was poured into 75 ml of water, treated with an excess of 20% sodium hydroxide, heated to boiling, filtered, and treated with a slight excess of 30% acetic acid. This precipitated the dihydroxyphenazine as minute yellow needles. Upon cooling 0.6 g of the substance was collected. The crude dihydroxyphenazine was purified by converting it into its diacetyl derivative (yielding 0.73 g of the diacetate with a m.p. of 230-232°), the diacetate being reconverted into 1,5-dihydroxyphenazine. Crystallization from benzene yielded 0.43 g of pure 1,5-dihydroxyphenazine (61% of the theoretical yield, based on the diethoxyphenazine used). Golden-yellow needles with a m.p. of 280-281°. Its mixed melting point with the preparation described above exhibited no depression.

1,6-Dihydroxyphenazine. 0.68 gram of 1,6-diethoxyphenazine, with a m.p. of 151-152° [7], was dissolved in 20 ml of 70% sulfuric acid. The reaction product was dealkylated and processed as the 1,5-dihydroxyphenazine. This yielded 0.48 g of nearly pure 1,6-dihydroxyphenazine (90% of the theoretical yield, based on the 1,6-diethoxyphenazine used). Brown-yellow needles, m.p. 305-306° with decomposition (in a sealed capillary). A small quantity of the 1,6-dihydroxyphenazine was recrystallized twice from a benzene-absolute alcohol mixture for analysis. This produced no change in the melting point.

Found %: N 12.82, 12.85. $C_{12}H_8O_2N_2$. Calculated %: N 13.2.

1,6-Diacetoxyphenazine was produced from the pure 1,6-dihydroxyphenazine. 0.1 g of the dihydroxyphenazine was refluxed with 2 ml of acetic anhydride for 2 hours. Then the reaction mixture was poured into 100 ml of water. Some time later 1,6-diacetoxyphenazine settled out as light-yellow needles. The precipitate was filtered out, washed with water, and crystallized from 50% alcohol. This yielded 0.1 g of pure 1,6-diacetoxyphenazine; light-yellow needles with a m.p. of 148-149°.

Found %: N 9.50. $C_{16}H_{12}O_4N_2$. Calculated %: N 9.46.

1,8-Dihydroxyphenazine. 0.6 gram of 1,8-diethoxyphenazine, with a m.p. of 174° [7], was heated with 8.5 ml of hydrobromic acid in a sealed tube to 130-140° for 5 hours. The reaction product received the same treatment as the 1,5-dihydroxyphenazine. The 1,8-dihydroxyphenazine was secured as 0.48 g of minute yellow needles (almost the quantitative yield, based on the 1,8-diethoxyphenazine employed). The 1,8-dihydroxyphenazine was purified by converting it into the diacetate. 0.48 gram of the dihydroxyphenazine was boiled with 5.5 ml of acetic anhydride for 30 minutes. The dihydroxyphenazine dissolved at first, the diacetate settling out of the boiling acetic anhydride as yellow leaflets some 10-15 minutes later. After the acetic anhydride had cooled, 0.55 g of the diacetoxyphenazine, with a m.p. of 257-268°, was recovered. The preparation was pure and did not require crystallization. The 1,8-dihydroxyphenazine was regenerated from it, 0.55 g of the 1,8-diacetoxyphenazine and 10 ml of alcohol being boiled with 40 ml of a 5% sodium hydroxide solution until the deposit dissolved completely. The subsequent processing of the phenazinolate was the same as that used for the phenazinolate of 1,5-dihydroxyphenazine. This yielded 0.44 g of the dihydroxyphenazine, which was recrystallized from benzene. We secured 0.4 g of pure 1,8-dihydroxyphenazine (84% of the theoretical yield, based on the 1,8-diethoxyphenazine used). Clusters of orange needles with a m.p. of 286-287° with decomposition (in a sealed capillary).

Found %: N 13.01, 13.02. $C_{12}H_8O_2N_2$. Calculated %: N 13.2.

The 1,8-diethoxyphenazine was dealkylated rapidly and smoothly with 70% sulfuric acid, the yield being high. 1.35 g of 1,8-diethoxyphenazine, with a m.p. of 194° was dissolved in 40 ml of 70% sulfuric acid. The solution was refluxed for 30 minutes over a paraffin bath at 180-182° and then poured into 150 ml of water, its subsequent processing being the same as that employed for the 1,5-dihydroxyphenazine. This yielded 1.02 g of 1,8-dihydroxyphenazine (97% of the theoretical yield, based on the diethoxyphenazine employed); its m.p. was 291-

292°. The preparation was purified by extraction with benzene in a Soxhlet apparatus, followed by crystallization from benzene. This yielded 0.83 g of the pure substance, which crystallized as clusters of orange needles; m.p. 296-297° (in a sealed capillary).

This preparation was used in preparing 1,8-diacetoxyphenazine, yellow leaflets with a m.p. of 257-258°. The preparations of 1,8-diacetoxyphenazine produced by dealkylating 1,8-diethoxyphenazine with hydrobromic and sulfuric acids had the same melting point, while their mixed melting point exhibited no depression.

The 1,8-diacetoxyphenazine was crystallized from alcohol for analysis. Yellow leaflets with a m.p. of 257-258°.

Found %: N 9.68, 9.50. $C_{16}H_{12}O_4N_2$. Calculated %: N 9.46.

SUMMARY

1,5-, 1,6-, and 1,8-dihydroxyphenazines have been synthesized by dealkylating the respective dialkoxyphenazines with hydrobromic acid or 70% sulfuric acid.

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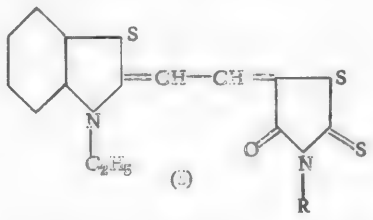
MEROCYANIN DYES THAT ARE DERIVATIVES OF RHODANINE

III. DIMETHINEMEROCYANINS – THE DERIVATIVES OF 3-AMINO- AND 3-DIACETYLAMINORHODANINE

Z. P. Sytnik, S. V. Natanson, M. V. Deichmeister, and L. D. Zhilina

We have previously shown [1] that substituting an alkyl group for the hydrogen atom attached to the nitrogen atom of the thiazolidine ring of the merocyanins – derivatives of rhodanine – such as (I) causes only a negligible shift of the dye's absorption maximum toward the longer wavelengths of the spectrum.



(I)

where R = H or C_6H_5.

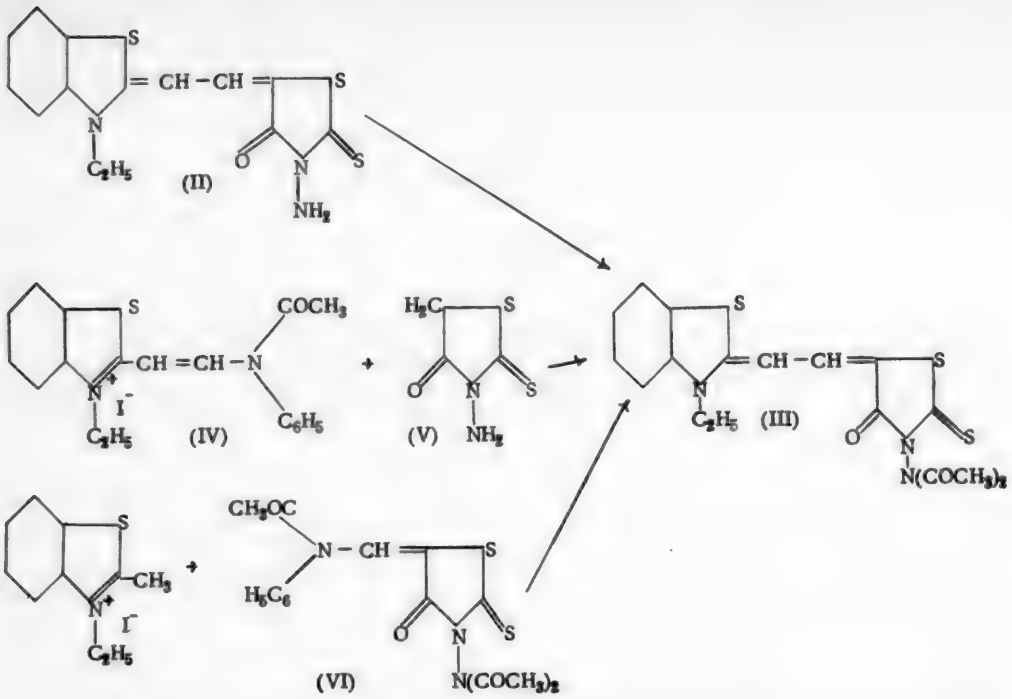
We were interested in determining the effect of substituting an amino group or an acylamino group for the hydrogen atom at that same position upon the properties of these dyes.

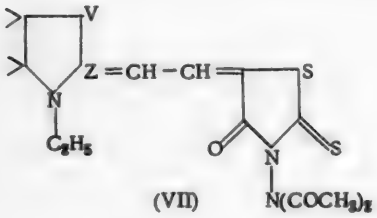
Of these dyes only a few amino substitution derivatives of the dimethinemerocyanins are mentioned in the patent literature [2]. The information given in these patents provides no idea at all of the properties of these compounds, however. We therefore synthesized analogous dyes with benzothiazole and benzoxazole (II) rings by condensing quaternary salts of acetanilinovinyl derivatives of these bases with 3-aminorhodanine in an alcoholic solution containing triethylamine [2]. Investigation of the photographic properties of these dyes has shown that the entrance of an amino group at the 3 position of the thiazolidine ring diminishes the sensitizing action, compared to that of the corresponding derivatives of the unsubstituted rhodanine.

No merocyanins with an acylated amino group at this position are described in the literature. Analogous dyes might have been expected to be formed when the respective amino substitution derivatives (II) are acylated. As a matter of fact, when we heated 3-amino-5-(3'-ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) (III) with acetic anhydride and anhydrous sodium acetate, we secured a dye that was the diacetylamino derivative (IV) according to its analysis data. We secured a high yield of the same dye by condensing the ethiodide of 2-(β-acetanilinovinyl)-benzothiazole (IV) with 3-aminorhodanine (V) in acetic anhydride containing anhydrous sodium acetate by boiling them together for a short time (5-7 minutes). Increasing the heating time lowers the product yield. Lastly, a third method of synthesizing this dye involves the reaction of 3-diacetylamino-5-(acetanilinomethylene)-rhodanine (VI) with 2-methylbenzothiazole ethiodide in an alcoholic solution containing triethylamine: (see diagram top of next page)

We are the first to have synthesized 3-diacetylamino-5-(acetanilinomethylene)-rhodanine (VI) from 3-aminorhodanine (V) and diphenylformamidine by heating the latter with acetic anhydride; adding sodium acetate greatly increases the yield of this compound.

The synethesized merocyanin (VII), in contrast to the amino substitution derivative (II), was highly soluble and possessed greater sensitizing action than the corresponding dyes derived from unsubstituted rhodanine. In this connection we thought it would be interesting to investigate as broadly as possible the optical and photographic properties of the dimethylmerocyanins, the derivatives of 3-diacetylaminorhodanine. With this in view, we synthesized analogous dyes containing the following residues: thiazoline, 5-methylthiodiazole-(1,3,4), benzothiazole, benzoxazole, benzoselenazole, 3,3-dimethylindolenine, β-naphthoxazole, 6,7-tetramethylene-benzothiazole, alpha and beta naphthothiazoles, and quinoline-(2 and 4) (VII).





where V = O, S, Se, −CH = CH−, or $C(CH_3)_2$,
and Z = carbon or the CH = CH − C = group
(when the latter group is present, there is no V).

The absorption maxima[1] of these dyes are given in Table 1, together with the maxima for the corresponding merocyanins derived from unsubstituted rhodanine and 3-aminorhodanine.

As we see from the figures in this table, introducing amino and diacetylamino groups at the 3 position of a thiazolidine residue has very little effect upon the color of these compounds. In most of the dyes we tested, moreover, we found a slight bathochromic shift (of some 2-6 mμ) of the same order of magnitude as found in the 3-ethylrhodanine [1], while the dyes that contain quinoline-(2 or 4) residues exhibit a slight displacement of the absorption maximum toward the shorter wavelengths (by some 4-6 mμ).

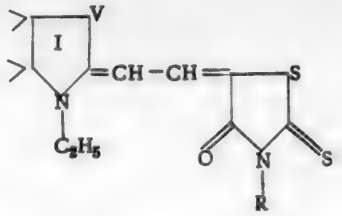
The slight influence of amino and diacetylamino groups upon the color of the merocyanins indicates that these groups interact negligibly with a polymethine chromophore.

The entrance of a diacetylamino group at the nitrogen atom of a thiazolidine residue increases efficiency over that of the dyes derived from unsubstituted rhodanine. The thiazoline, benzoxazole, 6,7-tetramethylenebenzothiazole, and α-naphthothiazole derivatives display exceptionally high sensitizing action. Somewhat lower, but still rather high, is the efficiency of dyes containing benzothiazole, β-naphthothiazole, and 5-methylthiodiazole-(1,3,4) residues. The derivatives of quinoline-(2 and 4) and of 3,3-dimethylindolenine are very weak sensitizers, however. As has been said above, introducing an amino group at this position has a negative effect upon the efficiency of this series of merocyanins.

All the dimethinemerocyanins – derivatives of 3-diacetylaminorhodanine – tested by us are very highly soluble in alcohol.

1) The absorption curves of alcoholic solutions of these dyes were measured with a Koenig-Martens spectrophotometer.

TABLE 1



Variable residue (I)	Absorption maximum (mμ)		
	R		
	H	$N(COCH_3)_2$	NH_2
Thiazoline	480	479	–
5-Methylthiodiazole-(1,3,4)	511	512	–
Benzoxazole	488	492	492
β-Naphthoxazole	502	507	–
Benzothiazole	520	526	526
6,7-Tetramethylenebenzothiazole	528	532	–
α-Naphthothiazole	536	542	–
β-Naphthothiazole	540	544	–
Benzoselenazole	522	528	–
3,3-Dimethylindolenine	500	505	–
Quinoline-(2)	564	558	–
Quinoline-(4)	612	608	–

EXPERIMENTAL

Synthesis of intermediates. 3-Aminorhodanine [3]. A suspension of 22.6 g of trithiocarbodiglycolic acid in 300 ml of water was treated with small portions of sodium carbonate until its reaction was slightly alkaline (about 15-16 g of Na_2CO_3), after which 14 g of hydrazine sulfate was added to the solution, and the latter was heated for 3 hours in a boiling water bath. The next day the precipitate was filtered out and washed with water and alcohol. The yield totaled 5.9-6.7 g (40-45% of the theoretical); m.p. 90-91°. The m.p. of the product was 92-92.5° after recrystallization from alcohol. Yellow needles, rather freely soluble in alcohol.

3-Diacetylamino-5-(acetylanilinomethylene)-rhodanine. A mixture of 1.8 g of 3-aminorhodanine, 2.82 g of diphenylformamidine, 1.02 g of anhydrous sodium acetate, and 20 ml of acetic anhydride was boiled for 20 minutes. Upon cooling a crystalline precipitate settled out, which was filtered out and washed with water and then with alcohol. The yield totaled 1.75 g (43% of the theoretical); m.p. 200-203°. The yield totaled 1.32 g (32% of the theoretical) after recrystallization from ethyl alcohol. Minute, light-yellow needles with a m.p. of 205-206°.

Found %: N 11.08. $C_{16}H_{15}O_4N_3S_2$. Calculated %: N 11.13.

Synthesis of Dyes that are Derivatives of 3-Aminorhodanine

3-Amino-5-(3'-ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4) [2]. A solution of 0.45 g of 3-aminorhodanine, 1.47 g of 2-(β-acetanilinovinyl)-benzothiazole ethiodide, and 0.42 g of triethylamine in 20 ml of absolute alcohol was boiled for 30 minutes. The next day the dye was filtered out and washed with alcohol and ether. The yield totaled 0.99 g (98.5% of the theoretical); m.p. 265° (with decomp.). Very slightly soluble in alcohol, so that it was refined by crystallization from pyridine. The yield was 0.7 g (69.5% of the theoretical). Brown needles with a green sheen; m.p. 276-277° (with decomp.).

Found %: N 12.32. $C_{14}H_{13}ON_3S_3$. Calculated %: N 12.22.

3-Amino-5-(3'-ethylbenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)[2]. This was synthesized, like the preceding dye, from 0.15 g of 3-aminorhodanine and 0.43 g of 2-(β-acetanilinovinyl)-benzoxazole ethiodide. The yield totaled 0.23 g (72.1% of the theoretical); m.p. 240-241° (with decomp.). Recrystalli-

TABLE 2

No.	Name of dye	Grams of I or II	Grams of specified quaternary salt	Condensation conditions: $(CH_3CO)_2O$ (ml)	Condensation conditions: CH_3COONa (g)
1	3-Diacetylamino-5-(3'-ethylbenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	I; 0.15 II; 0.38	III; 0.43 XI; 0.34	2 –	0.09 –
2	3-Diacetylamino-5-(3'-ethylbenzoselenazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	I; 0.15	IV; 0.5	2	0.09
3	3-Diacetylamino-5-(1'-ethyldihydroquinolylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	I; 0.15	V; 0.49	2	0.09
4	3-Diacetylamino-5-(1'-ethyldihydroquinolylidene-4'-ethylidene)-thiazolidinethion-(2)-one-(4)	I; 0.15	VI; 0.49	2	0.09
5	3-Diacetylamino-5-(1'-ethyl-3',3'-dimethylindolenylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	I; 0.15	VII; 0.45	2	0.09
6	3-Diacetylamino-5-(3'-ethyl-6',7'-tetramethylenebenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	II; 0.38	XV; 0.39	–	–
7	3-Diacetylamino-5-(3'-ethyl-6',7'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	II; 0.38	XII; 0.4	–	–
8	3-Diacetylamino-5-(3'-ethyl-4',5'-benzobenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	II; 0.38 I; 0.15	XIII; 0.4 X; 0.5	– 2	– 0.09
9	3-Diacetylamino-5-(3'-ethyl-4',5'-benzobenzoxazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	I; 0.15	IX; 0.53	2	0.09
10	3-Diacetylamino-5-[3'-ethyl-5'-methylthiodiazolinylidene-(1', 3',4')-2'-ethylidene]-thiazolidinethion-(2)-one-(4)	I; 0.15	VIII; 0.4	2	0.09
11	3-Diacetylamino-5-(3'-ethylthiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4)	II; 0.38	XIV; 0.3	3 ml of pyridine	

zation from methanol (1:3000) yielded 0.2 g (62.6% of the theoretical). Light red, thin needles with a m.p. of 242° (with decomposition).

Found %: N 12.99, 12.86. $C_{14}H_{13}O_2N_3S_2$. Calculated %: N 13.12.

Synthesis of Dyes that are Derivatives of 3-Diacetylaminorhodanine

We give below a complete description of the synthesis of a merocyanin containing a benzothiazole residue, which was produced by three methods. All the other dyes of this series were synthesized similarly, by the second or third method. We therefore give their synthesis conditions, yields, melting points and analysis results in Table 3 for the sake of brevity.[1] In this table, the following notation is used for the initial products: 3-aminorhodanine – I; 3-diacetylamino-5-(acetanilinomethylene)-rhodanine – II; the ethiodides of 2-(β-acetanilinovinyl)-benzoxazole – III, of 2-(β-acetanilinovinyl)-benzoselenazole – IV; of 2-(β-acetanilinovinyl)-quinoline – V; of 4-(β-acetanilinovinyl)-quinoline – VI; of 3,3-dimethyl-2-(β-acetanilinovinyl)-indolenine – VII; and of 5-methyl-2-(β-acetanilinovinyl)-thiodiazole-(1,3,4) – VIII; the ethyl p-tolusulfonates of 2-(β-acetanilinovinyl)-β-naphthoxazole – IX; of 2-(β-acetanilinovinyl)-β-naphthothiazole – X, of 2-methylbenzooxazole – XI, of 2-methyl-α-naphthothiazole – XII, of 2-methyl-β-naphthothiazole – XIII, and of 2-methylthiazolidine – XIV; and the ethylbenzenesulfonate of 2-methyl-6,7-tetramethylenebenzothiazole – XV.

[1]) No Table 3 appears in the original Russian text. The publisher.

Condensation conditions			Yield,	Ml of alcohol	Appearance	M.p. with	Per cent	Calculated	
C_2H_5OH (ml)	$(C_2H_5)_3N$ (ml)	Boiling time, minutes	percent of theoretical	used in crystallizing 1 g of dye	of dye	decomposition	N found	Empirical formula	Per cent N
–	–	5	66	300	Dark-pink needles	212-213	10.46; 10.61	$C_{13}H_{17}O_4N_3S_2$	10.46
7	0.14	30	46						
–	–	5	66	600	Dark-red prisms	232-233	8.91; 8.97	$C_{13}H_{17}O_3N_3S_2Se$	9.00
–	–	5	30	250	Lustrous green lamellae	202	10.18	$C_{20}H_{19}O_3N_3S_2$	10.15
–	–	5	35	250	Green prisms	224	10.10; 9.92	$C_{20}H_{19}O_3N_3S_2$	10.15
–	–	5	40	60	Bright-red prisms	200	9.90	$C_{21}H_{23}O_3N_3S_2$	9.78
10	0.14	30	60	1000	Dark-red prisms	238-239	8.84; 9.03	$C_{22}H_{23}O_3N_3S_3$	8.85
10	0.14	30	50	1300	Dark-red prisms	237-238	8.76	$C_{22}H_{19}O_3N_3S_3$	8.94
10	0.14	30	46	1500	Minute brown needles	242-243	8.8	$C_{22}H_{19}O_3N_3S_3$	8.94
–	–	5	42						
–	–	5	61	750	Light-red needles	255-256	9.39; 9.41	$C_{22}H_{19}O_4N_3S_2$	9.26
–	–	5	27	200	Lustrous red rhombic crystals	225-226	14.55 14.43	$C_{14}H_{16}O_3N_4S_3$	14.54
3 ml of pyridine		30	20	150	Lustrous orange lamellae	252-253	–	–	–

3-Diacetylamino-5-(3'-ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one-(4). This dye was synthesized in the three following ways.

a) A mixture of 0.167 g of 3-amino-5-(3'-ethylbenzothiazolinylidene-2'-ethylidene)-thiazolidinethion-(2)-one (4), 0.045 g of anhydrous sodium acetate, and 4 ml of acetic anhydride was boiled for 5 minutes. The yield of the dye was 0.15 g (71% of the theoretical) after recrystallization from alcohol. Violet needles with a green sheen; mp. 224-225° (with decomp.).

(b) A mixture of 0.45 g of 2-(β-acetanilinovinyl)-benzothiazole ethiodide, 0.15 g of 3-aminorhodanine, 0.09 g of anhydrous sodium acetate, and 2 ml of acetic anhydride was boiled for 5 minutes. The dye was washed with water, alcohol, and ether, yielding 0.33 g (80 % of the theoretical); m.p. 218-220° (with decomp.). Recrystallization from 150 ml of alcohol yielded 0.23 g (55 % of the theoretical); m.p. 224-225° (with decomp.).

c) A solution of 0.38 g of 3-diacetylamino-5-(acetanilinomethylene)-rhodanine, 0.305 g of 2-methylbenzothiazole ethiodide, and 0.14 ml of triethylamine in 7 ml of absolute alcohol was boiled for 30 minutes. The dye was recrystallized from alcohol yielding 0.25 g (60% of the theoretical); m.p. 224-225° (with decomp.). The yield of the dye did not exceed 30% of the theoretical when the reaction was carried out in pyridine.

Found %: N 9.99, 10.12. $C_{18}H_{17}O_3N_3S_3$. Calculated %: N 10.01.

SUMMARY

1. A new group of dimethinemerocynanins—derivatives of 3-diacetylaminorhodanine, containing thiazoline, 5-methylthiodiazole-(1, 3, 4), benzoxazole, benzothiazole, benzoselenazole, 3,3-dimethylindolenine, 6,7-tetramethylenebenzothiazole, β-naphthoxazole, alpha and beta naphththiazole, and quinoline-(2 and 4) residues, has been synthesized.

2. These dyes, in contrast to the corresponding derivatives of unsubstituted rhodanine and 3-aminorhodanine, are highly soluble.

3. The optical and photographic properties of these dyes have been investigated.

LITERATURE CITED

[1] M. V. Deichmeister, Z. P. Sytnik, and E. B. Lifshits, J. Gen. Chem. 22, 166 (1952)[1])

[2] Kodak Pathe, British Patent 490958; Eastman Kodak Co., U.S. Patent 2170805.

[3] B. Holmberg, J. Prak. Chem., 81, 451 (1910).

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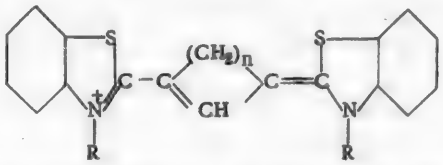
All-Union Institute of Cinema and Photographic Research

[1]) See Consultants Bureau English translation, p. 209.

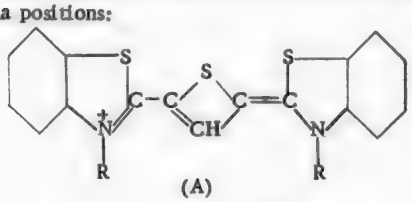
α, γ - EPOXYTHIACARBOCYANINS. I

I. K. Ushenko

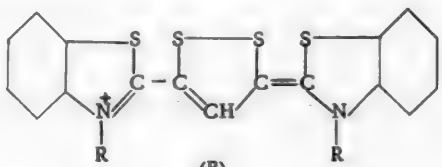
We have described [1] a series of thiacarbocyanins, the trimethine chromophore of which was part of the unsaturated ring:



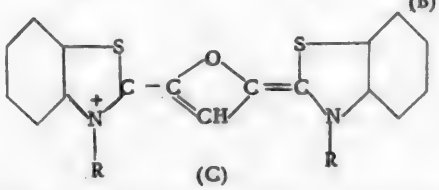
In the present research we set as our objective the introducing of sulfur and oxygen at the alpha and gamma positions:



(A)

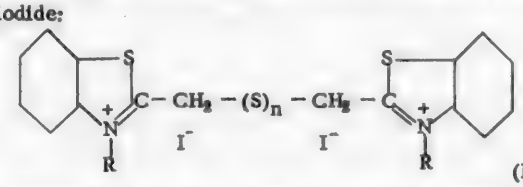


(B)



(C)

This was done by condensing thiodiglycolyl and dithiodiglycolyl chlorides with N-ethyl- and N-phenyl-o-aminothiophenol. The dichlorides were converted into the diiodides (I, II, III and IV) by the action of potassium iodide:



(I, II, III, IV)

The data on the diiodides (I, II, III, and IV) are set forth in Table 1.

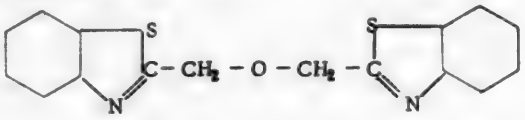
TABLE 1

No.	R	n	Melting point (with decomposition)
I	C_2H_5	1	146°
II	C_6H_5	1	198
III	C_2H_5	2	123
IV	C_6H_5	2	178

We assumed that heating these diquaternary salts with orthoformic ester in pyridine or acetic anhydride would yield dyes containing sulfur at the alpha and gamma positions (A) and (B). The condensation of the diquaternary salts with orthoformic ester in pyridine or acetic anhydride, however, yielded dyes that contained no sulfur at the alpha and gamma positions. Investigation of the properties (analysis, absorption curves in alcoholic solution, melting points) of mixed samples of the synthesized dyes indicated that when the salts (I) and (III) were heated with orthoformic ester, 3,3'-diethylthiacarbocyanin iodide was produced, while the salts (II) and (IV) yielded 3,3'-diphenylthiacarbocyanin iodide, which has been described earlier.

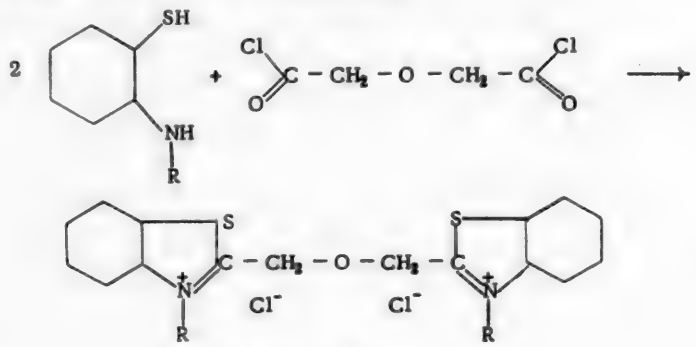
We have not tried to ascertain the mechanism of this condensation, involving the loss of sulfur atoms.

We found that it is fairly easy to synthesize cyanin dyes containing oxygen at the alpha and gamma positions (C). When o-aminothiophenol was heated with diglycolic acid, we got bis-[benzothiazolyl-(2)] oxide: large white scales, m.p. 105°:



We succeeded in transforming this base into a diquaternary salt by heating it with the ethyl ester of p-toluenesulfonic acid. The yield of the quaternary salt was extremely low.

The corresponding diquaternary salts are readily formed by condensing benzene solutions of diglycolyl chloride with N-ethyl-and N-phenyl-o-aminophenols:



R = C_2H_5, C_6H_5

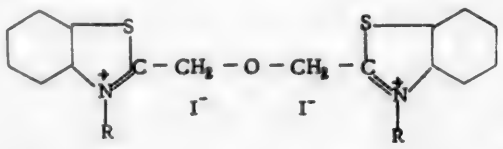
These salts were converted into the diiodides (V and VI), listed in Table 2, by the action of potassium iodide.

TABLE 2

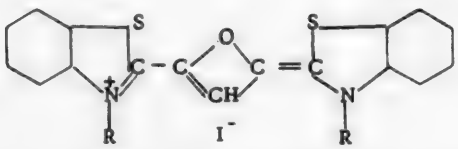
No.	R	Melting point	Appearance
V	C_2H_5	208°	Yellow needles
VI	C_6H_5	214	Large brick-red needles

It should be noted that the diquaternary salts remained brightly colored, in spite of their being refined by crystallization from alcohol or water and boiling with activated charcoal.

When a yellow alcoholic or pyridine solution of the salt (V) was exposed to the action of a weak alkali, the solution reddened, while the action of alkali upon the orange solution of the salt (VI) turned the solution blue. The quaternary salts are condensed fairly readily with orthoformic ester in acetic anhydride. No dyes are produced in pyridine. The two dyes (VII) and (VIII) listed in Table 3 were synthesized.



(V, VI)



(VII, VIII)

The absorption maxima of the dyes (VII) and (VIII) differ but little from the maxima of the corresponding carbocyanins, in which the oxygen atom in the four-membered ring has been replaced by a methylene group

TABLE 3

No.	R	Absorption maximum, mμ	$E_{max} \cdot 10^{-4}$
VII	C_2H_5	555*	13.2
VIII	C_3H_5	575	11.5

(R = C_2H_5 – 560 mμ, R = C_3H_5 – 568 mμ). The synthesized dyes hardly fluoresce at all and readily decolorize alkalies and acids. Alcoholic solutions of the dyes are completely decolorized within 1-2 hours in bright sunlight. Their analogs, which contain a methylene group at the 8, 10 position, resist the action of light and alkalies rather well.

I. P. Dmitrenko, A. V. Stetsenko, and E. N. Rubtsova participated in the experimental portion of the present research.

EXPERIMENTAL

The acid chlorides of thiodiglycolic acid [2] and diglycolic acid [3] were prepared from the acids and phosphorus pentachloride.

The acid chloride of dithiodiglycolic acid [4] was prepared from dithiodiglycolic acid and thionyl chloride.

Bis-[benzothiazolyl-(2)]oxide. 5 grams of diglycolic acid (1 mole) was heated with 9.3 g of o-aminothiophenol (2 mole) in a sealed tube for 20 hours on an oil bath at 140-145°. The reaction product was processed with alkali and then with water. Double recrystallization from alcohol yielded large white scales, m.p. 105°, the yield being 6.2 g, or 55% of the theoretical.

Found %: N 9.12. $C_{10}H_{12}ON_2S_2$. Calculated %: N 8.97.

Diquaternary Salts

The procedure employed in preparing the diquaternary salts was the standard one. Equimolecular quantities of N-ethyl- or N-phenyl-o-aminothiophenol and the acid chloride were dissolved in anhydrous benzene, and the two solutions were mixed together. The benzene was decanted from the diquaternary salt produced, the residue being dissolved in hot water and decolorized with activated charcoal, after which the hot aqueous solutions of the chlorides were converted into diiodides by the action of potassium iodide. The salts were crystallized from alcohol or water.

Bis-[benzothiazolyl-(2)-methyl] sulfide diethiodide (I). This was synthesized from 5.7 g of N-ethyl-o-aminothiophenol and 3.5 g of thiodiglycolyl chloride. Yellow crystals from alcohol, which turned dark upon standing. M.p. 146° with decomposition. 27% of the theoretical yield.

Found %: I 38.42. $C_{20}H_{28}N_2S_3I_2$. Calculated %: I 39.68.

Bis-[benzothiazolyl-(2)-methyl] sulfide diiodophenylate (II). This was synthesized from 7.5 g of N-phenyl-o-aminothiophenol and 3.5 g of thiodiglycolyl chloride. Yellow crystals from alcohol, which darken upon standing. M.p. 198° with decomposition. 30% of the theoretical yield.

Found %: I 33.05. $C_{28}H_{22}N_2S_3I_2$. Calculated %: I 34.50.

Bis-[benzothiazolyl-(2)-methyl] disulfide diethiodide (III). This was synthesized from 2.2 g of N-ethyl-o-aminothiophenol and 1.6 g of dithiodiglycolyl chloride. Yellow crystals from alcohol. M.p. 122° with decomposition. 32% of the theoretical yield.

Found %: S 18.81. $C_{20}H_{28}S_4N_2I_2$. Calculated %: S 19.04.

Bis-[benzothiazolyl-(2)-methyl] disulfide diiodophenylate (IV). This was synthesized from 2.9 g of N-phenyl-o-aminothiophenol and 1.6 g of dithiodiglycolyl chloride. Minute yellow crystals. M.p. 178° with decomposition. 23% of the theoretical yield.

Found %: S 16.53. $C_{28}H_{22}N_2S_4I_2$. Calculated %: S 16.67.

Bis-[benzothiazolyl-(2)-methyl] oxide diethiodide (V). This was synthesized from 2 g of N-ethyl-o-aminothiophenol and 1.1 g of diglycolyl chloride. Yellow crystals from alcohol. M.p. 208° with decomposition. 43% of the theoretical yield.

Found %: I 40.23. $C_{20}H_{28}ON_2S_2I_2$. Calculated %: I 40.73.

Bis-[benzothiazolyl-(2)-methyl] oxide diiodophenylate (VI). This was synthesized from 2 g of N-phenyl-o-aminothiophenol and 0.9 g of diglycolyl chloride. Elongated red needles. M.p. 214° with decomposition. 61% of the theoretical yield. The preparation strongly irritates the mucous membrane of the nose.

Found %: I 35.22. $C_{28}H_{22}ON_2S_2I_2$. Calculated %: I 35.27.

Dyes

3,3'-Diethyl-8,10-epoxythiacarbocyanin iodide (VII). 0.4 g of bis-[benzothiazolyl-(2)-methyl] oxide diethiodide was boiled for 1 hour with 0.4 g of orthoformic ester and 2.5 ml of acetic anhydride. The dye was precipitated with ether. Recrystallization from alcohol yielded minute dark crystals. M.p. 198° with decomposition. The yield was 0.10 g, or 31% of the theoretical.

Found %: I 24.87. $C_{21}H_{19}ON_2S_2I$. Calculated %: I 25.09.

3,3'-Diphenyl-8,10-epoxythiacarbocyanin iodide (VIII). 1 g of bis-[benzothiazolyl-(2)-methyl] oxide diiodophenylate was boiled for 45 minutes with 1 g of orthoformic ester and 4 ml of acetic anhydride. The dye was precipitated with water. Recrystallization from alcohol yielded crystals with a bronze sheen. M.p. 178° with decomposition. The yield was 0.25 g, or 30% of the theoretical.

Found %: I 20.98. $C_{29}H_{19}ON_2S_2I$. Calculated %: I 21.09.

SUMMARY

1. Two diquaternary salts have been synthesized by condensing diglycolyl chloride with N-ethyl- and N-phenyl-o-aminothiophenol. Reacting them with orthoformic acid yielded two new dyes — α,β-epoxythiacarbocyanins.

2. Condensation of o-aminothiophenol with diglycolic acid yielded a new base — bis-[benzothiazolyl-(2)-methyl] oxide.

3. Four diquaternary salts were synthesized from N-ethyl- and N-phenyl-o-aminothiophenol and the thiodiglycolyl and dithiodiglycolyl chlorides; reacting these salts with orthoformic ester in acetic anhydride or pyridine detached sulfur atoms and gave rise to thiacarbocyanins that were unsubstituted in the trimethine chain.

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DYES WITH ANTIPYRINE RINGS. II

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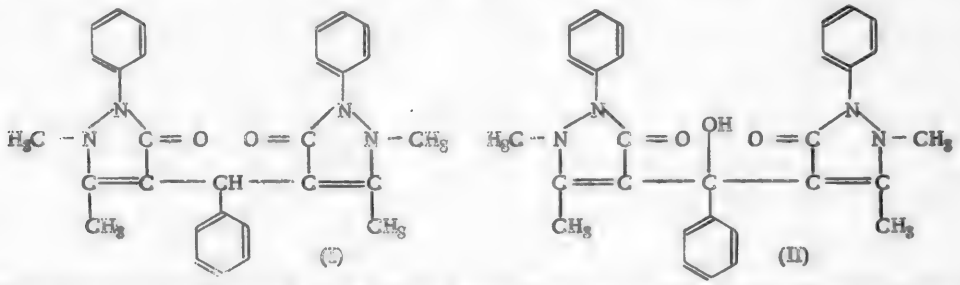
A few years ago we synthesized a new group of dyes, whose properties resembled those of basic triphenylmethane dyes, by oxidizing the condensation products of aromatic aldehydes with two molecules of antipyrine [1]. The simplest representative of this group of dyes, formed by the oxidation of diantipyrylphenylmethane, was obtained as a nitrate and was called antipyrine orange.

When an aqueous solution of antipyrine orange is reacted with an alkali solution, we get diantipyrylphenylcarbinol (II), which reconstitutes the dye when treated with acid.

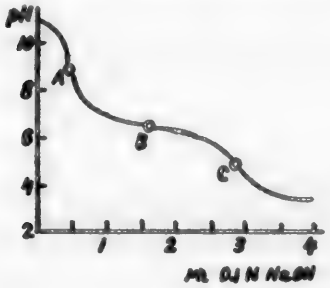


(I) (II)

Diantipyrylphenylcarbinol is much more soluble in water than, say 4,4'-tetramethyldiaminotriphenylcarbinol, so that we can prepare a 0.001 molar aqueous solution of diantipyrylphenylcarbinol. We found that aqueous solutions of diantipyrylphenylcarbinol are readily colored, even if the solution contains a slight excess of free alkali.

The antipyrylphenylcarbinol solution, which contained a small percentage of sodium hydroxide, was titrated potentiometrically. In titrating this solution potentiometrically we found that after all the sodium hydroxide had been neutralized by adding hydrochloric acid, the solution pH, observed immediately after a new portion of hydrochloric acid had been added, gradually rose for a few minutes until it reached a certain value, after which it remained unchanged. Thus, the reaction of diantipyrylphenylcarbinol with hydrochloric acid, which is accompanied by the production of a dye, takes place at a quite perceptible velocity. There are two points of inflection on the curve plotted from the pH values of the solution under titration.

The first point of inflection on this curve (Point A) represents the titration endpoint of the free sodium hydroxide in the solution, while the second (Point B) represents the titration endpoint of the diantipyrylphenylcarbinol. These findings indicate that titration of diantipyrylphenylcarbinol requires one equivalent of hydrochloric acid, the basicity constant of diantipyrylphenylcarbinol being $10^{-7.6}$.



Our observations have led us to conclude that the ionization of diantipyrylphenylcarbinol in an aqueous solution is accompanied by the splitting out of a hydroxyl ion and the constitution of a colored organic cation. Inspection of the structure of diantipyrylphenylcarbinol bears out the correctness of this conclusion.

In view of the fact that the properties of dyes containing antipyryl rings resemble those of the triphenylmethane dyes, it must be supposed that the carbinol compounds produced when triphenylmethane dyes are reacted with an alkali are likewise ionized similarly in aqueous solutions.

EXPERIMENTAL

In every experiment the solution pH was measured in a pH-meter using glass and calomel electrodes.

1. 0.0797 g of antipyryl orange was dissolved in 100 ml of water. The solution had a pH of 4.80 (temperature 17°).

2. 0.1124 g of diantipyrylphenylcarbinol was dissolved in 3.1 ml of 0.1N hydrochloric acid (T = 0.00363), the resultant solution being mixed with 193 ml of water. 3.5 ml of a 0.1N solution of sodium hydroxide (T = 0.00408) was added to the hydrochloric acid solution. The solution was gradually decolorized, the carbinol base remaining in solution. Back titration was commenced 2 hours later. After the next portion of hydrochloric acid had been added, readings were made every 4-5 minutes. The temperature of the solution under titration was 17° (Table 1).

TABLE 1

Ml of 0.1N HCl added	Galvanometer reading, millivolts	Ml of 0.1N HCl added	Galvanometer reading, millivolts
–	94	1.6	64
0.1	94	1.7	64
0.2	93	2.0	62
0.3	92	2.4	60
0.4	86	2.6	57
0.5	75	2.7	56
0.6	72	2.8	51
0.7	69	2.9	47
0.8	68	3.0	46
1.2	65	3.2	44
1.5	64	4.0	41

The titration curve is reproduced in the figure. Constitution of the dye required 2.3 ml of 0.1N hydrochloric acid (T = 0.00363). Calculation indicated that 2.3 ml of a carbinol solution with a pH of 8.9 was required; the pH of a solution constituting an equimolecular mixture of the dye and the carbinol was 6.6; the pH of the dye solution was 4.8. The basicity constant of diantipyrylphenylcarbinol, calculated from the pH at the point B, $K_B = 10^{-7.6}$.

3. 0.1542 g of antipyrine orange was dissolved in a mixture of 4 ml of a 0.1N solution of hydrochloric acid (T = 0.00358) and 196 ml of water, 8 ml of a 0.1N solution of sodium hydroxide (T = 0.00404) was added, and the mixture was set aside to stand. One hour later the solution of the carbinol base was back titrated with a 0.1N solution of hydrochloric acid. Readings were made 4-5 minutes after each portion of hydrochloric acid was added (Table 2).

TABLE 2

Ml of 0.1N HCl added	Galvanometer reading, millivolts
1.4	77
1.7	75
2.0	74
2.3	73
2.6	71
2.9	69

TABLE 3

Ml of 0.1N NaOH solution added	Galvanometer reading, millivolts	
	After the addition of NaOH	20 minutes later
–	69	–
0.3	93	72
0.6	93	73
0.9	93	74
1.2	93	76

After 2.9 ml of 0.1N hydrochloric acid had been added, back titration with 0.1N sodium hydroxide solution was commenced, the solution pH being read immediately after each portion of alkali had been added and then again 20 minutes later (Table 3).

SUMMARY

1. In aqueous solution the ionization of the carbinol compounds produced by the action of an alkali upon triphenylmethane dyes is accompanied by the splitting out of a hydroxyl ion and the formation of a colored organic cation.

2. The basicity constant of diantipyrylphenylcarbinol is $10^{-7.6}$ (17°).

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several observations made by M. M. Shemyakin and his associates on the hydrolytic cleavage of a double bond [9].

Having been working for a long time on analogous condensations and being greatly interested in the problem of whether beta hydroxydicarboxylic acids exist, we endeavored to repeat A. Gakhokidze's research. We observed a slight rise in temperature (to 8-12°) when diethyl malonate was reacted with anhydrous acetone and pulverized potassium hydroxide, chilled to 0° with absolute ether present. The precipitate gradually changed during the course of 2-3 hours, turning from a finely powdered one to a scaly form. No further changes were found. The reaction mass was set aside to stand for 2, 3, 10, and more days. Subsequent treatment, by the method recommended by A. Gakhokidze as well as by other methods, yielded nothing but the unchanged malonate and acid monoethyl ester of malonic acid. The scaly precipitate proved to be the potassium salt of this acid monoethyl malonate. A similar precipitate was secured when diethyl malonate was reacted with pulverized potassium hydroxide in absolute ether containing no acetone.

Nor did a repetition of the condensations with ethyl formate and ethyl acetate prove to be any more successful. We were unable to recover the respective beta hydroxy acids.

EXPERIMENTAL

Experiment 1. 116 g of anhydrous acetone and 160 g of diethyl malonate (the constants of which were exactly the same as those given in the literature) were dissolved in 200 ml of absolute ether chilled to 0°, and the solution was agitated while 50 g of finely powdered potassium hydroxide was added portionwise. The temperature of the reaction mass rose to 8-12°. Chilling was continued for 2 hours, after which the mass was set aside to stand at room temperature for 10 days (or 2, 3, 15 days, etc.), with agitation from time to time. Then the reaction mass was dissolved in water, the supernatant oil being removed and the aqueous layer washed with ether; the extract was combined with the removed layer, and the whole dried with sodium sulfate, after which the ether was driven off and the residue distilled in vacuo. This yielded 50 g of a distillate with a b.p. of 102-103° at 26 mm (98-99° at 23 mm); n_D^{24} 1.4115 (the diethyl ester of malonic acid). Saponification with alkali yielded malonic acid with an m.p. of 134-135°, which exhibited no depression of the melting point when mixed with an analytical sample.

Experiment 2. This reaction was similar. The precipitate was filtered out, washed with acetone, and dried. This yielded 100 g of scaly white crystals. The ether and acetone were driven out of the mother liquor, and the residue distilled in vacuo. This yielded 50 g of the malonic ester (see Experiment 1). The precipitate was dissolved in absolute methanol and saturated with anhydrous hydrogen chloride until no more precipitate was thrown down. The precipitate was filtered out, and the methanol driven off in a low vacuum. This left behind a light-yellow oil, which was water-soluble and was converted by heat into ethyl acetate, with a b.p. of 76-78°.

Analysis of the potassium salt: 0.0920, 0.1850 g substance: 0.0472, 0.0945 g K_2SO_4. Found %: K 22.93, 22.92. $C_5H_7O_4K$. Calculated %: K 22.93.

Experiment 3. 12.5 grams of pulverized potassium hydroxide was added portionwise, with agitation, to a solution of 40 g of diethyl malonate in 50 ml of absolute ether chilled to 0°. The subsequent processing and results were the same as those cited in Experiment 2.

We were unable to secure the corresponding hydroxy acids (hydroxyisobutyric and β-hydroxyisovaleric acid) by condensing acetone with ethyl formate and ethyl acetate in ether solution at 0° in the presence of pulverized potassium hydroxide.

SUMMARY

1. Repeating the A. Gakhokidze experiments on the synthesis of beta hydroxy acids does not bear out the results he describes.

2. The constants of the initial malonic ester cited in Gakhokidze's paper do not agree with the constants of diethyl or dimethyl malonate.

3. The constants of diethyl isopropylidenemalonate cited by the authors do not agree with those described for this substance.

4. The method of producing hydroxy acids proposed by Gakhokidze and Guntsadze, involving saponification by an alcoholic alkali, is inapplicable, owing to the ease with which these compounds are cleaved.

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